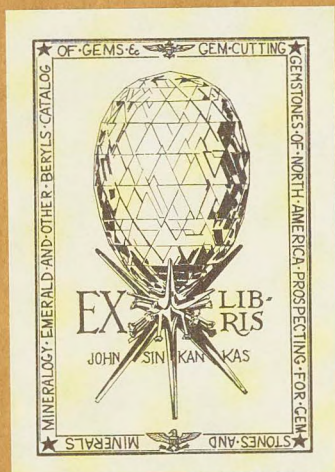


MINERALOGICAL CHEMISTRY

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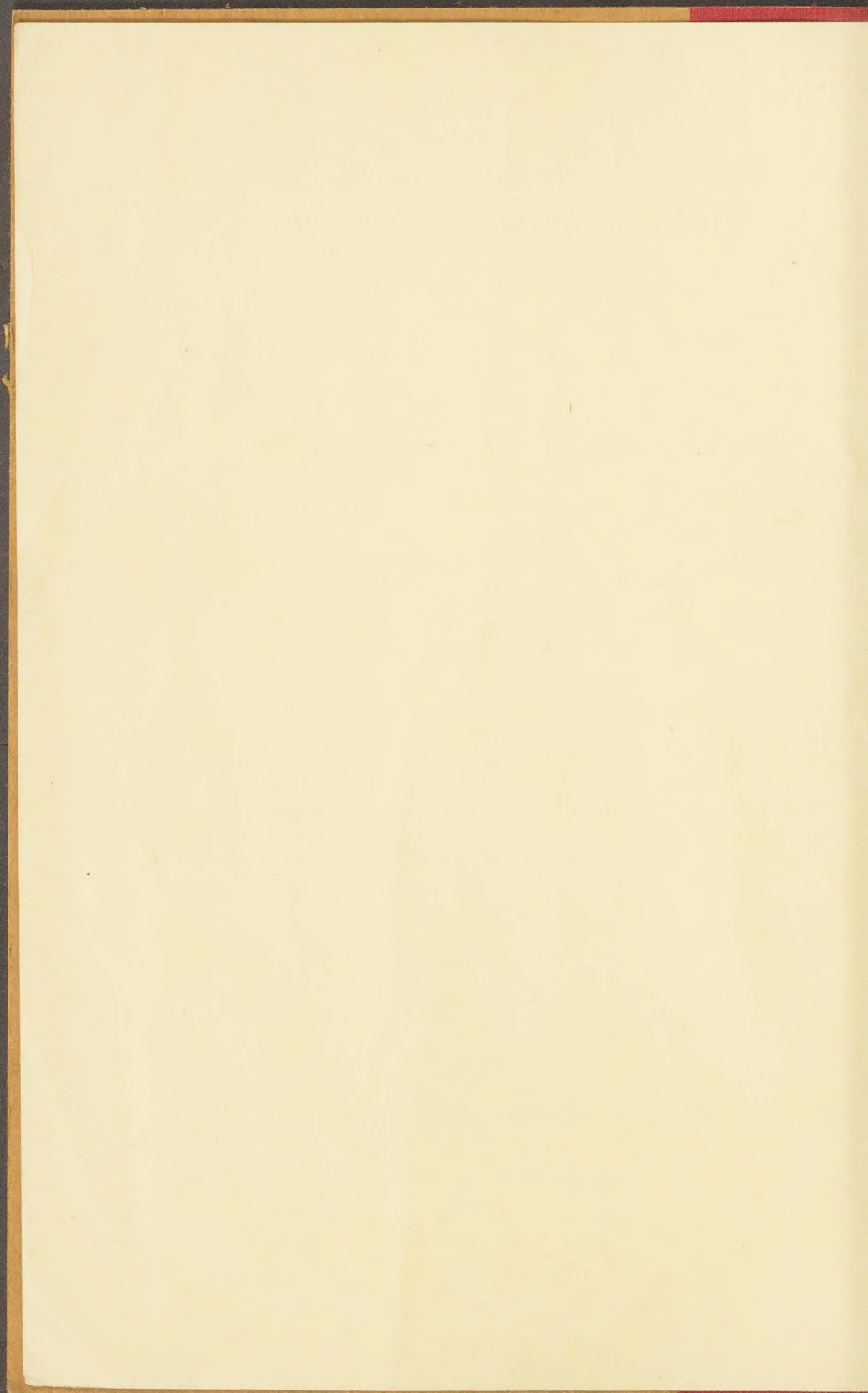


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MINERALOGICAL CHEMISTRY.

BY
L. J. SPENCER, M.A., Sc.D., F.R.S.

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MINERALOGICAL CHEMISTRY.

Geochemistry.

BISCHOF's classical work on "Chemical Geology" dating from 1847, seems to have been almost forgotten, but there is now a revival in the study of this comprehensive subject under the name "Geochemistry." Recent books are: a new (fifth) edition of F. W. Clarke's well-known "Data of Geochemistry"¹; W. Vernadsky, "La Geochimie" (Paris, 1924); and, in Russian, A. E. Fersman, "Geochemistry of Russia."² The readable and very suggestive book by Vernadsky contains the following chapters: I, General considerations on geochemistry; II, Silicon as silicates in the earth's crust; III, Carbon and living matter; IV, The radioactive chemical elements. Fersman's book deals with "topomineralogy," the distribution of chemical elements, and the accumulation and association of elements in certain places; genetic mineralogy in relation with genetic types and cycles. European Russia is divided into twelve geochemical regions or provinces.

An elaborate paper by F. W. Clarke and H. S. Washington on "The composition of the earth's crust"³ collects together their previous conclusions and gives the details on which these conclusions are based. The final calculations give for the average composition of the solid crust to a depth of ten miles, including also the hydrosphere and atmosphere, the following percentages: O, 49.52; Si, 25.75; Al, 7.51; Fe, 4.70; Ca, 3.39; Na, 2.64; K, 2.40; Mg, 1.94; H, 0.88; Ti, 0.58; Cl, 0.188; P, 0.12; C, 0.087; Mn, 0.08; S, 0.048; Ba, 0.047; Cr, 0.033; N, 0.030; F, 0.027; Zr, 0.023; Ni, 0.018; Sr, 0.017; V, 0.016; Ce, Y, 0.014; sum of remainder 0.042%. It is seen that 99.5% of the crust consists of thirteen elements and but few common rock-forming minerals. These, together with those listed above and some others, are classed as "petrogenic" elements. "Metallogenic" elements are Cu, Zn, Ga, Ge, As, Se, Br and the others falling below them in the periodic table; they are of sporadic occurrence and are found only under

¹ *Bull. U.S. Geol. Survey*, 1924, No. 770, 841 pp.

² Part I of Vol. I (Petrograd, 1922); [*Min. Mag. (Abstr.)*, 1925, 2, 415]. The work is to be completed in three volumes, each consisting of several parts.

³ *Prof. Paper U.S. Geol. Survey*, 1924, No. 127; *A.*, 1925, ii, 63 (compare *Ann. Report*, 1923, 20, 261).

certain conditions as workable deposits of economic value. The compounds of these two "natural" groups of chemical elements, as represented in nature by minerals, are considered in detail. Petrogenic elements form mostly oxides and oxygen-salts, whilst metallogenic elements form mostly sulphides, arsenides, and sulpho-salts.

H. S. Washington wanders farther afield and considers the radial distribution of certain elements in the earth's interior.⁴ From a consideration of the composition of meteorites and rocks, the velocity of earthquake waves at different depths, and the density and compressibility of minerals and rocks, he draws conclusions bearing on the distribution of matter within the earth.⁵ The following zones are deduced: central core of nickel-iron, corresponding with meteoric iron (3,400 km. thick); lithosporic shell consisting of patches of silicates in a sponge of metal, corresponding with pallasites (700 km.); ferrosporic shell, corresponding with meteoric stones (700 km.); peridotitic shell (1,540 km.); basaltic shell (40 km.); and granitic shell or surface crust (20 km.). From the calculated chemical composition, volume, and mass of each of these zones, the composition of the earth as a whole is deduced as: Fe, 39.76 (31.82 as free metal, and 7.94 in silicates); O, 27.71; Si, 14.53; Mg, 8.69; Ni (free), 3.16; Ca, 2.52; Al, 1.79; S, 0.64; Na, 0.39; Co, 0.23; Cr, 0.20; K, 0.14; P, 0.11; Mn, 0.07; C, 0.04; Ti, 0.02; total, 100.00. It is noted that there is an excess of iron for combination with silicon and oxygen.

The chemistry of the earth's core has been further considered by L. H. Barnett,⁶ his calculations being based on the known densities of the earth as a whole and its crust and of the chemical elements, together with Washington's data for the average chemical composition of the crust. An irregular core of metallic substances ("metallic fusion"), probably more or less mixed with silicates, is estimated at about 77.5% of the whole, whilst an irregular shell of silicates ("slag"), more or less mixed with metal, constitutes the remaining 22.5%. This core is estimated to consist of Fe, 90%; Ni, Co, and Cu, 7%; the remaining 3% including gold and platinum at 0.003%. G. Tammann considers that between the metallic core and the silicate crust there is a zone of sulphides.⁷

It is to be noted that speculations on the chemical composition of the interior of the earth are based largely on a comparison of the composition of terrestrial rocks and meteorites. We may so pass

⁴ *J. Washington Acad. Sci.*, 1924, **14**, 435; *A.*, 1925, ii, 234.

⁵ *Amer. J. Sci.*, 1925, [v], **9**, 351; *A.*, ii, 591. ⁶ *J. Geol.*, 1924, **32**, 615.

⁷ *Z. anorg. Chem.*, 1924, **131**, 96; 1924, **134**, 269; *A.*, 1924, ii, 163, 493 (compare *Ann. Report*, 1923, **20**, 262).

from geochemistry to cosmochemistry. Both of these aspects of the subject are dealt with by A. E. Fersman in a small book entitled "Chemical Elements of the Earth and the Cosmos."⁸ He considers the laws of distribution and migration of the chemical elements in the earth and in the cosmos, and traces a connexion between such distribution and their place in the periodic system and their atomic structure. It is pointed out that everywhere—in the earth's crust, in meteorites, the sun, planets, comets, and stars—there is a preponderance of elements of the helium atomic group, namely those with atomic weights divisible by 4 and up to atomic number 28 (Ni). P. N. Chirvinsky⁹ has calculated an average composition for cosmic matter from statistical data of the weights and number of meteorites of different types that have been observed to fall on the earth's surface during the period 1492 to 1921. The percentage composition arrived at may be expressed by the formula $M_4Si_2O_7$, which may also be written as a mixture of orthosilicate, metasilicate, and free metal, $M_2SiO_4 + MSiO_3 + M$, where M is a collective metal with mean atomic weight 40.58. Metals and metalloids are present in very nearly equal proportions by weight. This is taken to represent a pseudo-element, "cosmium," with equivalent atomic weight 25.59. An interesting and suggestive essay, entitled "The evolution and disintegration of matter," has been written by F. W. Clarke.¹⁰

In the several recent papers descriptive of individual meteorites an outstanding feature is the discovery in 1921 of an enormous mass of meteoric iron in the desert of Adrar, at about 45 km. south-west of Chinguetti in Mauretania, French West Africa. As reported by A. Lacroix,¹¹ it measures 100 metres in length and 40 metres in height, and is perhaps 160,000 cubic metres in volume. Containing about 20% of silicates, it represents a new type of meteorite intermediate between the siderites and pallasites; further, the silicate portion consists largely of hypersthene rather than olivine.

Amongst the mineral constituents of meteorites, quartz has been mentioned as present in the St. Mark's meteoric stone.¹² Of the phosphates sparingly present in certain stones, it is now found that merrillite has the composition $Na_2O, 3CaO, P_2O_5$, and is thus distinct from any known terrestrial mineral.¹³ In one stone it was found associated with chlor-apatite. Hydrocarbons ("bitumen") have

⁸ Peterburg, 1923 (in Russian); [*Min. Mag. (Abstr.)*, 1924, 2, 256].

⁹ *Astronomische Nachrichten*, 1924, 222, 103; [*Min. Mag. (Abstr.)*, 1925, 2, 389].

¹⁰ *Prof. Paper U.S. Geol. Survey*, 1924, No. 132-D, 51.

¹¹ *Compt. rend.*, 1924, 179, 309; *A.*, 1924, ii, 693.

¹² G. P. Merrill, *Amer. Min.*, 1924, 9, 112.

¹³ E. V. Shannon and E. S. Larsen, *Amer. J. Sci.*, 1925, [v], 9, 250; *A.*, ii, 321.

occasionally been recorded in meteorites; and the suggestion is now made that these may have been formed by the action of water on carbides after the arrival of the meteorites on the earth's surface.¹⁴

A problem to which some attention has lately been given, but which still remains unsolved, is that of the origin of *tektites*.¹⁵ This general term includes the moldavites or "bottle-stone" found in river-gravels in Bohemia and Moravia. These consist of a clear glass, and being of a rich green colour they have been used as gemstones under the names "pseudo-chrysolite" and "water-chrysolite." They are remarkable for their corrugated and deeply sculptured surfaces. At one time they were thought to be artificial, the products of an ancient glass-making industry, and this view is still held by some authors. Other kinds of tektites are the australites or "obsidianites," found in large numbers loose on the surface of the ground in certain parts of Australia and Tasmania; and the billitonites found in river-gravels and tin-gravels in Billiton and other places in the East Indies. These consist of dark green or black glass with glossy surface, and are of curious button-like, dumb-bell, and other shapes with surface markings in concentric rings. They have been thought to be of volcanic origin, the curious shapes being acquired when molten drops of lava were shot out from volcanoes. But there are no recent volcanoes in Australia. The suggestion made by F. E. Suess in 1900 that tektites are of meteoric origin was only slowly accepted, but now there are many adherents to this view. None has been observed to fall. If they did fall they evidently came down in showers, like the meteoric stones which fell at Holbrook, Arizona, in 1912, when more than 14,000 stones were picked up. The main difficulty, however, is that presented by the chemical composition of these glassy bodies. They are high in silica, 70% to 88%, with only little lime and alkalis. They thus differ in composition from artificial and volcanic glasses and very widely from any recognised meteorites.

Constitution of Silicates.

The papers on this subject are increasing in number, but it must be said that no real advance appears to be made. Various theories are being put forward and each is tested serially for different groups of minerals. Much ingenuity is displayed in attempting to explain all cases by any one theory. The mica group has been studied most, and samples of the different types of formulæ that have been proposed are quoted below.

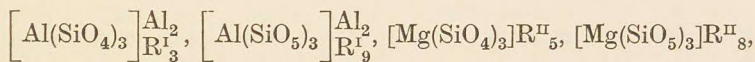
¹⁴ P. E. Spielmann, *Nature*, 1924, **114**, 276; *A.*, 1924, ii, 867.

¹⁵ V. Goldschmidt, *Beitr. Kryst. Min.*, 1924, **2**, 148. A series of abstracts of recent papers in *Min. Mag. (Abstr.)*, 1922, **1**, 406-9.

B. Gossner doubts the existence of complex molecules corresponding with the empirical formulæ of silicates, for example KAlSi_3O_8 for orthoclase; and he expresses the composition by the combination, analogous to double salts, of certain simple and stable molecules, such as SiO_3Ca , Al_2O_3 , AlO_2H , SiO_2 , etc. In addition to the papers mentioned in the last report, he has continued the series¹⁶ with the groups of chlorites, "brittle micas," monoclinic pyroxenes and amphiboles, alkali-amphiboles, babingtonite, gehlenite-melilitite group, and micas. For example, the "building scheme" (Bauplan) for the pyroxenes is based on the complex (double salt) $\text{SiO}_3\text{Mg}, \text{SiO}_3\text{Ca}$, in which SiO_3Mg is replaceable by Al_2O_3 or $\text{SiO}_3(\text{Fe}, \text{Mn})$, and SiO_3Ca by SiO_3Mg . The following are some of the formulæ he gives for the micas:

Muscovite . . .	$[\text{SiO}_2, \text{SiO}_3\text{K}_2, \text{Al}_2\text{O}_3], 4\text{SiO}_2, 4\text{AlO}_2\text{H}.$
Biotite . . .	$[\text{SiO}_3\text{K}_2, \text{SiO}_3\text{Mg}], 3\text{SiO}_3\text{Mg}, 3\text{AlO}_2\text{H}.$
Lepidolite . . .	$[\text{SiO}_3\text{K}_2, \text{SiO}_3\text{Li}_2], 4\text{SiO}_2, 4\text{AlOF}.$

According to the theory of J. Jakob silicates are referred to the prototypes $[\text{SiO}_4]\text{R}_4^{\text{I}}$, $[\text{SiO}_5]\text{R}_6^{\text{I}}$, and $[\text{SiO}_6]\text{R}_8^{\text{I}}$, with or without added SiO_2 groups. For the micas he postulates the following "part-molecules" (Teilmoleküle):



and $[\text{Mg}(\text{SiO}_5\text{SiO}_2)_3]\text{R}_{18}^{\text{II}}$. He gives detailed analyses, together with density and optical determinations, for eight specimens of mangano-phyllite (a variety of biotite containing some manganese) from Sweden.¹⁷ As an example of the type of formula, the following (in which, curiously, manganese does not appear) is deduced from one of the analyses:

$$50.07 \left[\text{Al}(\text{SiO}_4)_3 \right]_{\text{H}_{0.866}}^{\text{Al}_2 \text{K}_{2.134}} + 39.04 \left[\text{Mg}(\text{SiO}_5)_3 \right]_{\text{H}_{2.962}}^{\text{Mg}_{6.519}} + 10.89 \left[\text{Mg}(\text{SiO}_5\text{SiO}_2)_3 \right]_{\text{H}_{2.962}}^{\text{Mg}_{6.519}}.$$

W. Kunitz¹⁸ has made a noteworthy attempt to correlate the physical and optical characters with the chemical composition for minerals of the mica group. Only few data, in which all the determinations were made on the same sample of material, are available from the literature. Thirty-two new analyses were therefore made

¹⁶ *Centr. Min.*, 1924, 97, 129, 257; 1925, *Abt. A.*, 1, 39, 73; *Z. Krist.*, 1924, 60, 76, 302, 361; 1925, 61, 538; *Chemie der Erde*, 1925, 2, 103; *A.*, ii, 821.

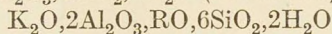
¹⁷ *Z. Krist.*, 1925, 61, 155.

¹⁸ *Jahrb. Min. Beil.-Bd.*, 1924, 50, 365.

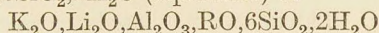
of micas of various kinds, and in many cases the density and optical constants were also determined. It is shown that in biotite, etc., the estimation of water is often too low, due to the reaction $2\text{FeO} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}_2\text{O}_3 + \text{H}_2$. To obviate this, the mineral was heated with chlorate and the gases passed over platinised asbestos. Three main isomorphous groups of micas are recognised: I, alumina-micas or the muscovite series, in which Al is replaceable to a limited extent (up to 10%) by Fe^{III} . II, magnesia-iron micas or the biotite series, in which Mg and Fe^{II} are completely replaceable. III, lithia-micas or lithionites; here a special tervalent group $[\text{2Li, Si}]$, denoted as "Le," is completely replaceable by Fe^{II} . A summary of the results with formulæ of the hypothetical end-members is quoted below. They show that with increasing iron there is a corresponding, often linear, increase in the density and in the refractive indices. The refractive indices are to some extent also modified by the complete isomorphous replacement of F and OH. Partial isomorphous replacements are also Si—Ti, Si—Al, Al—Cr—Mn, and K—Na (but not K—H and Al—Mg, as required by some theories). All micas can be considered to contain the fundamental molecule KAlSiO_4 (kaliophilite) with the addition of molecules corresponding with kaolin, serpentine, and chlorites.

	End-members.	$n(\alpha)$.	$n(\beta)$.	$n(\gamma)$.	2E.	d .
Muscovite	$\text{KH}_2\text{Al}_3(\text{SiO}_4)_3$	1.5514	1.5810	1.5873	80° 40'	2.802
Al: Fe^{III} = 10:1	↓	1.5719	1.6105	1.6148	58 10	2.885
(not known)	$\text{KH}_2\text{Fe}^{\text{III}}_3(\text{SiO}_4)_3$	—	—	—	—	—
Phlogopite	$\text{KH}_2\text{AlMg}_3(\text{SiO}_4)_3$	1.5440	—	1.578	?	2.791
Biotite	↓	—	—	—	—	—
Lepidomelane	$\text{KH}_2\text{AlFe}^{\text{II}}_3(\text{SiO}_4)_3$	1.629	—	(1.68)	?	3.340
Lepidolite	$\text{KH}_2\text{Al}_2\text{Le}(\text{SiO}_4)_3$	1.5290	1.5520	1.5558	78 20	2.801
Zinnwaldite	↓	1.5485	1.5745	1.5792	50 6	2.97
Protolithionite	$\text{KH}_2\text{AlFe}^{\text{II}}_3(\text{SiO}_4)_3$	1.592	—	1.625	0	3.305

A. F. Hallimond¹⁹ calculates from published analyses of the "acid" micas the molecular proportions on the basis $(\text{Si, Ti})\text{O}_2 = 600$. In the soda- and potash-micas $\text{K}_2\text{O} + \text{Na}_2\text{O}$ is then near 100. The molecular proportions of R_2O_3 plotted against RO give points along a line from $\text{K}_2\text{O}, 3\text{Al}_2\text{O}_3, 6\text{SiO}_2, 2\text{H}_2\text{O}$ (muscovite) to



(phengite), showing a replacement of R_2O_3 by RO, as previously suggested for glauconite.²⁰ In the lithia-micas $\text{SiO}_2 = 600$, $\text{K}_2\text{O} = 100$, $\text{Li}_2\text{O} = 100$, and R_2O_3 plotted against RO gives two series: $\text{K}_2\text{O}, \text{Li}_2\text{O}, 2\text{Al}_2\text{O}_3, 6\text{SiO}_2, 2\text{H}_2\text{O}$ (lepidolite) to



(cryophyllite), and lepidolite to $\text{K}_2\text{O}, \text{Li}_2\text{O}, 2\text{Al}_2\text{O}_3, 3\text{RO}, 6\text{SiO}_2, 2\text{H}_2\text{O}$

¹⁹ *Min. Mag.*, 1925, 20, 305; *A.*, ii, 819.

²⁰ *Ibid.*, 1922, 19, 330; *A.*, 1922, ii, 861.

the tetrahedron, and are representative of two three-component systems, muscovite-polyolithionite-protolithionite and muscovite-protolithionite-phengite, which are referred to as the muscovite and lepidolite systems, respectively. The optical data of these micas are represented by contour lines on the same tetrahedron. The octophyllites and the heptaphyllites are the two main groups of the micas between which there are no mixed crystals; the former are usually dark-coloured and the latter are usually light-coloured, and there are important differences in their optical characters.

This idea of "volume isomorphism" in the silicates had been previously considered by F. Zambonini²² and by E. T. Wherry²³ in connexion with the well-known case of albite ($\text{NaAlSi}_3\text{O}_8$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$)—this pair forming a complete series of mixed crystals in the plagioclase feldspars. Here NaSi and CaAl are evidently the replacing pairs. The sum of their atomic volumes²⁴ as calculated from W. L. Bragg's (1920) atomic radii are approximately the same, and the two atoms taken together will fit into the same crystalline structure. Further, it is to be noticed that the sum of the valencies of the two pairs of replacing atoms is the same. A similar case is given by the isomorphism of diopside ($\text{CaMgSi}_2\text{O}_6$) and acmite ($\text{NaFe}^{\text{III}}\text{Si}_2\text{O}_6$), and also by calcite (CaCO_3) and sodium nitrate (NaNO_3). This, however, seems to be only a re-statement of the fact pointed out by J. D. Dana as long ago as 1850 that the molecular volumes (molecular weight/density) are approximately equal for these pairs of isomorphous substances.

The same replacement of NaSi by CaAl as in the plagioclases is also worked out by A. N. Winchell²⁵ for the several minerals of the zeolite group. For example, the published analyses of thomsonite are plotted on a square at the four corners of which are the lime and soda molecules $\text{Ca}_3\text{Al}_6\text{Si}_{10}\text{O}_{32}\cdot\text{Aq}$, $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}\cdot\text{Aq}$, $\text{Ca}_5\text{Al}_{10}\text{Si}_6\text{O}_{32}\cdot\text{Aq}$ and $\text{Na}_{10}\text{Al}_{10}\text{Si}_6\text{O}_{32}\cdot\text{Aq}$, the varying ratios $\text{Al}_2\text{O}_3:\text{SiO}_2$ and $\text{CaO}:\text{Na}_2\text{O}$ being shown along the two co-ordinates. The analyses fall along a curved line between the points $\text{Na}_4\text{Ca}_8\text{Al}_{20}\text{Si}_{20}\text{O}_{80}\cdot 25\text{H}_2\text{O}$ and $\text{Na}_7\text{Ca}_5\text{Al}_{17}\text{Si}_{23}\text{O}_{80}\cdot 20\text{H}_2\text{O}$, which are regarded as the end-members of an isomorphous series. Quite different results have been arrived at for thomsonite by other authors. E. T. Wherry,²⁶ by plotting Na_2O against SiO_2 , obtains two well-marked clusters: one around the composition $\text{NaCa}_2\text{Al}_5\text{Si}_5\text{O}_{20}\cdot 6\text{H}_2\text{O}$, corresponding with thom-

²² *Atti (Rend.) R. Accad. Lincei*, 1922, [v], **31**, (i), 295; *Amer. Min.*, 1923, **8**, 81.

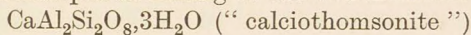
²³ *Amer. Min.*, 1922, **7**, 113.

²⁴ E. T. Wherry, *ibid.*, 1923, **8**, 1, calculates the atomic volumes: O = 1, H = 5, Si = 7, Al = 11, Ca = 22, Na = 23×10^{-24} c.c.

²⁵ *Ibid.*, 1925, **10**, 88, 112, 145, 166.

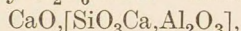
²⁶ *Ibid.*, 1923, **8**, 121; 1925, **10**, 342.

sonite proper; and the other around $\text{Na}_2\text{Ca}_3\text{Al}_8\text{Si}_9\text{O}_{34} \cdot 9\text{H}_2\text{O}$, corresponding with faroelite. Each of these minerals possesses definite optical constants, and there is no range of variation, as would be the case in an isomorphous series. Deviations shown by some analyses are ascribed to mechanical mixtures with natrolite or mesolite. From the same series of published analyses S. G. Gordon²⁷ calculates the molecular ratios with $\text{Na}_2\text{O} = 1$; CaO then ranges from 1.00 to 5.97. When the total $\text{Na}_2\text{O} + \text{CaO}$ is plotted against SiO_2 and against H_2O the analyses are grouped along straight lines, which indicate the isomorphous mixing of the end-members

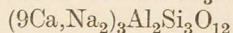


and $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot \text{H}_2\text{O}$.

In other groups a similar wide diversity of opinion is also shown in recent papers. The melilite group was the subject of much experimental work at the Geophysical Laboratory in Washington.²⁸ B. Gossner,²⁹ however, regards as improbable the existence of such complex molecules and he traces a connexion between these tetragonal minerals and the monoclinic ("pseudo-tetragonal") pyroxenes. They are regarded as double compounds $\text{CaO} + \text{pyroxene}$ of the form $\text{CaO} \cdot [\text{SiO}_3\text{Ca}, \text{SiO}_3\text{Mg}]$, where SiO_3Mg is replaceable by Al_2O_3 , and $\text{Si}_2\text{O}_6\text{MgCa}$ by $\text{Si}_2\text{O}_6\text{AlNa}$. Gehlenite is written



and melilite as $2\text{CaO} \cdot [\text{Si}_2\text{O}_6\text{MgCa}, \text{Si}_2\text{O}_6\text{AlNa}]$. A. N. Winchell,³⁰ on the other hand, regards the molecules $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (gehlenite) and $\text{Ca}_2\text{MgSi}_2\text{O}_7$ (åkermanite) as well-established end-members of the group; but the hypothetical molecule $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ or



(sarcosite) he thinks is doubtful. The last may be split up into $\text{Ca}_2\text{Al}_2\text{SiO}_7$, $\text{Ca}_3\text{Si}_2\text{O}_7$, and SiO_2 . Including Si with R, these, as well as gehlenite and åkermanite, reduce to the general type R_5O_7 ; and they are therefore regarded as replaceable in the space-lattice of melilite. The excess of silica is supposed to fall into the interatomic spaces, thereby producing a considerable effect on the density, but little effect on the refractive indices.

Correlations of the optical constants with the chemical composition in isomorphous groups of minerals have been shown graphically on plots of various kinds by several authors, especially by A. N. Winchell³¹ in a series of papers on the pyroxenes, amphiboles, scapolites, and micas. Accurately determined data, all determined

²⁷ *Proc. Acad. Nat. Sci. Philadelphia*, 1924, **76**, 103; *A.*, 1924, ii, 868.

²⁸ *Ann. Report*, 1920, **17**, 213; 1923, **20**, 268.

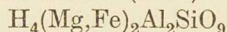
²⁹ *Chemie der Erde*, 1925, **2**, 103; *A.*, ii, 821.

³⁰ *Amer. J. Sci.*, 1924, [v], **8**, 375; *A.*, ii, 152.

³¹ *Ibid.*, 1923, [v], **6**, 504; 1924, **7**, 287; 1925, **9**, 309, 415; *Amer. Min.*, 1924, **9**, 108; 1925, **10**, 335.

on the same sample of material, and thus suitable for purposes of correlation, have been given by H. S. Washington and H. E. Merwin,³² and by N. Sundius³³ for various pyroxenes and amphiboles. Unfortunately, with many recent mineral analyses the authors omit to state the density of the material analysed. Many published mineral analyses have been made solely for purposes of identification, and these should not be taken into account when attempting to arrive at the constitution of minerals.

The chemical composition of isomorphous groups of silicates (tourmaline, chlorite, mica) were studied by E. S. Fedorov³⁴ by graphically plotting the analyses. With three or four independent variables, different methods of plotting involving a special geometry were devised. The composition of various silicate minerals is represented by points on or in a "chemical tetrahedron," and the positions of these points are expressed geometrically by symbols resembling crystallographic indices. At the four corners of the tetrahedron are grouped the univalent, bivalent, trivalent, and quadrivalent elements, respectively³⁵ (oxygen being omitted). The symbol for quartz will then be (0001), for corundum (also hæmatite) (0010), spinel (0120), albite (1013), anorthite (0122), etc. The three main types of micas are (1011), (0445), and (4403), corresponding respectively with muscovite, biotite, and phlogopite. These points are all on the surface of the tetrahedron. Points representing the more complex chlorites fall inside the tetrahedron, and all in a plane with the indices ($\bar{6}$ 456). Amesite,



or (4221), shows the relation $\bar{6} \times 4 + 4 \times 2 + 5 \times 2 + 6 \times 1 = 0$; and the same holds with the other chlorites, clinocllore (8523), delessite (5222), corundophyllite (20·11·8·6), etc.

The System Alumina-Silica.

The trimorphous minerals andalusite, fibrolite, and kyanite, with the composition Al_2SiO_5 or $\text{Al}_2\text{O}_3, \text{SiO}_2$, are well known, and in certain rocks they are of abundant occurrence in nature. Kyanite is typically a product of the dynamic (or pressure) metamorphism of rocks, whilst andalusite and fibrolite are often the products of contact (or thermal) metamorphism. Neither andalusite nor kyanite has been prepared artificially; and it is now said that the supposed artificial fibrolite is not $\text{Al}_2\text{O}_3, \text{SiO}_2$, but $3\text{Al}_2\text{O}_3, 2\text{SiO}_2$.

³² *Amer. Min.*, 1923, 8, 63, 104, 215.

³³ *Geol. För. Förh.*, 1924, 46, 154.

³⁴ *Bull. Acad. Sci. Russie*, 1918, [vi], 12, 615, 625, 645, 1891; [*Min. Mag. (Abstr.)*], 1925, 2, 425].

³⁵ Similar to Fig. 2 in *Ann. Report*, 1923, 20, 267, but with univalent elements at one corner in place of MgO or CaO.

There is thus a recurrence of the once vexed question of the composition of fibrolite. In the old text-books on mineralogy bamlite, bucholzite, fibrolite, monrolite, sillimanite, wörthite, and xenolite have at one time or another ranked as distinct species. Analyses showed widely varying ratios of alumina to silica, due, as now known, to the intimate intermixture of silica with the finely fibrous and dense material (and the same is true of the artificial product). These minerals are now all united under the species fibrolite, and modern text-books are all agreed on the formula $\text{Al}_2\text{O}_3, \text{SiO}_2$, although not on the mineralogical name to be applied to the species. The name Faserkiesel dates from 1792 and its equivalent fibrolite from 1802; whilst the name sillimanite, now in common use in petrography, was first given by G. T. Bowen in 1824.

The system alumina-silica was studied experimentally in the Geophysical Laboratory at Washington in 1909,³⁶ and the conclusion then arrived at was that the only compound is Al_2SiO_5 . The crystalline product was identified with fibrolite, the crystallographic and optical characters agreeing with those of the natural mineral (although it was noticed at the time that the crystals were mixed with glass and that they had refractive indices slightly lower than those of natural fibrolite).

Later work in the Geophysical Laboratory by N. L. Bowen³⁷ and his collaborators, in 1924, showed that this artificial product, eliminating the glass, has the composition $3\text{Al}_2\text{O}_3, 2\text{SiO}_2$. And it is further asserted that all "fibrolite" previously prepared artificially has the same composition. A mixture of alumina and silica in equal molecular proportions was found to crystallise from fusion as a mixture of $3\text{Al}_2\text{O}_3, 2\text{SiO}_2$ and cristobalite (SiO_2) or glass. Above 1810° , this breaks down into corundum (Al_2O_3) and liquid. It was also found that natural fibrolite, when heated at 1545° , breaks down to $3\text{Al}_2\text{O}_3, 2\text{SiO}_2$ and a highly siliceous glass. This compound $3\text{Al}_2\text{O}_3, 2\text{SiO}_2$ is also described by the same authors as a natural mineral under the name *mullite*. This was found as microscopic crystals, which had earlier been referred to fibrolite, in the buchites (inclusions of fused slaty rocks in igneous intrusions) from the Island of Mull in Scotland. None of the three minerals with the composition $\text{Al}_2\text{O}_3, \text{SiO}_2$ could be obtained artificially, and they are ignored in the equilibrium diagram of the system $\text{Al}_2\text{O}_3\text{-SiO}_2$; but in view of their abundant occurrence in nature, their existence can-

³⁶ E. S. Shepherd, G. A. Rankin, and F. E. Wright, *Amer. J. Sci.*, 1909, [iv], 28, 293; *Ann. Report*, 1909, 6, 202. G. A. Rankin and F. E. Wright, *ibid.*, 1915, 39, 1; *Ann. Report*, 1915, 12, 243.

³⁷ N. L. Bowen and J. W. Greig, *J. Amer. Ceramic Soc.*, 1924, 7, 238; N. L. Bowen, J. W. Greig, and E. G. Zies, *J. Washington Acad. Sci.*, 1924, 14, 183; *A.*, 1924, ii, 416.

not very well be denied. The conditions operating in nature are evidently very different from those in the laboratory and in the study.

No essential difference is shown between the crystallographic and physical characters of fibrolite and mullite. Both are orthorhombic with the same prism angle and the highly perfect cleavage parallel to the brachy-pinakoid. The optical orientation is the same for both, and also the wide difference between the birefringences $\gamma-\alpha$ and $\beta-\alpha$ on the planes (010) and (001), respectively. They also give identical spectra by the X-ray powder method.³⁸ The only difference is that the refractive indices of mullite (α 1.642, γ 1.654) are slightly lower than those of fibrolite (α 1.657, γ 1.677). When, however, the crystals of mullite contain small amounts of impurities (Fe_2O_3 and TiO_2) the values, α 1.661 and γ 1.682, actually exceed those for fibrolite.

We have here a very unusual case showing an anomalous relation between chemical composition and crystalline structure. Crystals in which there are isomorphous replacements are expected to be very similar in their geometrical and physical properties; but here we have identity of properties with a different molecular ratio of $\text{Al}_2\text{O}_3 : \text{SiO}_2$. No similar case can be called to mind. Malachite [$\text{CuCO}_3, \text{Cu}(\text{OH})_2$] and chessylite [$2\text{CuCO}_3, \text{Cu}(\text{OH})_2$], though both monoclinic, are very different in structure and all their properties; matlockite ($\text{PbCl}_2, \text{PbO}$) and mendipite ($\text{PbCl}_2, 2\text{PbO}$) are tetragonal and orthorhombic, respectively; alamosite (PbO, SiO_2) and barysilite ($3\text{PbO}, 2\text{SiO}_2$), monoclinic and hexagonal; and many other similar examples could be cited. It would seem that some mistake has been made. The existence of fibrolite ($\text{Al}_2\text{O}_3, \text{SiO}_2$) cannot be denied.³⁹ If the existence of mullite as $3\text{Al}_2\text{O}_3, 2\text{SiO}_2$ is confirmed, the suggestion may be made that the physical characters assigned to it are really those of fibrolite. Many examples can be collected from the literature of cases in which the chemical composition has been determined on material of one kind, whilst the crystallographic properties have been determined on material of another kind.⁴⁰ Difficulties of this kind are frequently met with when dealing with finely crystallised mixtures.

The artificial reproduction of fibrolite or mullite is of mineralogical and chemical interest, but it is also of considerable economic importance in the manufacture of refractory materials and ceramic ware.

³⁸ This is confirmed by F. Rinne, *Z. Krist.*, 1925, **61**, 113.

³⁹ Crystals of fibrolite from which excellent gems have been cut have recently been described (*Min. Mag.*, 1920, **19**, 107).

⁴⁰ For example, the characters of the so-called orthorhombic or β -tin, as quoted in the text-books, were determined on orthorhombic crystals of stannous sulphide (*Min. Mag.*, 1921, **19**, 113).

It has been prepared on a large scale in a crystalline form by smelting aluminous rocks or minerals with coke in a cupola furnace.⁴¹ A review of the literature on the presence and development of artificial "sillimanite" in ceramic ware has been given by A. B. Peck.⁴² He also describes an occurrence of andalusite-rock in California, which is mined with an output of about 70 tons per week, the material being used in the manufacture of the porcelain cores of sparking plugs for automobiles. This mineral when heated at about 1390° is transformed into a parallel aggregate of fibres of mullite with interstitial glass, the density changing from 3.29 to 3.20. Since the volume change accompanying this transformation is only slight, the powdered mineral can be mixed with the clay body before firing. Kyanite is transformed at about 1370° into an irregular interlocking aggregate of mullite fibres with interstitial glass, there being here a greater change in volume (d 3.59 to 3.09). J. W. Greig⁴³ finds that this decomposition takes place at no definite temperatures, but is lowest for kyanite and highest for fibrolite. Above 1050°, only mullite is stable. The decomposition of kyanite and of andalusite is accompanied by an absorption of heat.

The stability relations of the three minerals andalusite, fibrolite, and kyanite have been studied by F. Neumann.⁴⁴ The specific heat and heat of solution (in 40% hydrofluoric acid) were determined for each, and also for the mixture of mullite and silica prepared from equal molecular proportions of alumina and silica. These data are applied in Nernst's heat theorem, and from the "A-U" (work-energy) diagram for the pair andalusite-fibrolite, it is concluded that fibrolite is the stable modification up to 1487°, and that andalusite is stable above this temperature. Kyanite as compared with fibrolite is completely unstable. Direct experiments show, however, that when heated at 1200° andalusite changes into mullite and glass; and kyanite shows the same change at 1400°.

Colour in Minerals.

Minerals that possess no colour of their own may, when well developed as single crystals, be perfectly colourless, clear, and transparent. Examples are the rock-crystal variety of quartz and the Iceland-spar variety of calcite. Often, however, the crystals are cloudy or opaque, due to inclusions of foreign matter. If this foreign matter consists of ferric hydroxide, the crystal may be

⁴¹ A. Malinovsky, *J. Amer. Ceram. Soc.*, 1920, **3**, 40; *Trans. Ceram. Soc.*, 1920, **19**, 140.

⁴² *Amer. Min.*, 1924, **9**, 123; 1925, **10**, 253; *J. Amer. Ceram. Soc.*, 1925, **8**, 407.

⁴³ *J. Amer. Ceram. Soc.*, 1925, **8**, 465; *A.*, ii, 987.

⁴⁴ *Z. anorg. Chem.*, 1925, **145**, 193; *A.*, ii, 849.

yellow, brown, or red, as often seen in quartz and calcite. Or again, crystal aggregates may be intermixed with impurities of various kinds, as in the multi-coloured jaspers and marbles. In such cases the cause of the colour is obvious and is shown by an ordinary chemical analysis. In other cases the crystal, though brightly coloured, may still be perfectly clear and transparent: for example, the amethyst, cairngorm, and citrine varieties of quartz, which are used as gem-stones; wine-yellow and violet calcite; brilliant sky-blue halite (rock-salt); and fluorite with its wide range of delicate colours. The colour of emerald and ruby has been attributed to traces of chromium (and in the artificial gem-rubies the colour is produced by the addition of chromic oxide). But in the majority of cases chemical analysis gives no clue as to the cause of the colour. This "dilute colouring" is due, according to the theory of C. Doelter, to the presence of a colloidal substance, and the different colours to the degree of dispersity or size of the particles of the colloid. But it may be doubted if colloids can exist in a solid crystalline medium. Crystals of organic compounds are capable of taking up traces of aniline dyes, and it may be suggested that minerals are merely dyed with traces of inorganic (in some cases organic) colouring matter. Some colours are clearly due to the interference of light brought about by structures in the stone (as in mother-of-pearl); and it is evident that the colours of minerals cannot be all explained by any one theory. The main difficulty is presented by certain minerals that exhibit remarkable changes in colour with change in temperature and when exposed to radium emanations, ultra-violet rays, cathode-rays, X-rays; and further, these changes are often accompanied by striking luminescent and phosphorescent effects in the mineral. Such changes have been studied by C. Doelter and others, but with very erratic results, and the same effects cannot always be repeated.

The various colour-varieties of quartz have recently been investigated in detail by E. F. Holden.⁴⁵ The colour of citrine he attributes to sub-microscopic particles of ferric hydroxide. Deep-amber coloured material was found to contain 0.026% Fe_2O_3 , whilst specimens with a pale yellowish tinge contained only 0.008% to 0.011%. Further, the darker colour was closely imitated with a colloidal solution of ferric hydroxide of the same degree of concentration, and the absorption-spectrum of light transmitted through this solution is identical with that of citrine. Pink crystals of quartz contained 0.043% Fe_2O_3 and showed microscopic inclusions of hæmatite. This colour was imitated by mixing finely powdered hæmatite with sodium silicate. Rose-quartz showed in 27 analyses

⁴⁵ *Amer. Min.*, 1923, 8, 117; 1924, 9, 75, 101; 1925, 10, 127, 203; *A.*, 1924, ii, 620.

of material from various localities a loss on ignition of 0.10—0.25% and solid impurities 0.13—0.29%. Small amounts of MnO , TiO_2 , Fe_2O_3 , CoO , Li_2O , and Al_2O_3 were estimated. The manganese ranges with the depth of colour (pale pink to deep pink) from 0.0002 % to 0.0006% as MnO ; and the conclusion is drawn that the colour is due to some manganic (Mn^{III}) compound. The absorption-spectrum and dichroism of rose-quartz are similar to those of substances known to contain Mn^{III} . Rose-quartz is decolorised at about 575° , and when exposed to radium it becomes smoky. Contrary to the statement in books on precious stones, the colour is not affected by sunlight.⁴⁶ The rose colour has been imitated in a silica gel by the addition of manganic borate (0.01—0.02% MnO). A rose-quartz with a bluish tinge contained 0.029% TiO_2 and showed under the microscope abundant inclusions of fine hairs of rutile, to which the bluish colour is ascribed. Smoky-quartz is immediately decolorised at 440° and slowly at 235° , and the colour is restored by radium radiations. The small amounts of iron, titanium, and manganese shown by analysis bear no relation to the depth of the colour; whilst uranium (UO_3 0.001—0.006%) and free silicon are most abundant in darker specimens. Free silicon was estimated by boiling the finely powdered mineral in aqua regia, when colloidal silicic acid passes into solution; the darker specimens gave Si 0.01%. The conclusion is drawn that the smoky colour is due to the scattering of light by atoms of free silicon and that these have been liberated by the action of radioactive substances. Amethyst is often associated with iron minerals and it frequently contains inclusions of goethite and hæmatite. It is decolorised at 26% and the violet colour is restored by radium. Darker-coloured specimens become yellow when ignited and then show the same absorption-spectrum as citrine. Manganese and titanium are present in only small amounts, which do not vary with the depth of colour. The average amounts of Fe_2O_3 in specimens free from visible inclusions range with the colour from 0.007% to 0.14%. The colour of amethyst is similar to that of ferric ammonium alum and is evidently due to some ferric compound, which when heated breaks down to ferric hydroxide.

The yellow and purple calcites from Joplin, Missouri, have been studied by W. P. Headdon⁴⁷ with special reference to the phosphorescent and luminescent phenomena which they display. When the mineral is heated at 250° for twenty minutes, many of these properties are destroyed and the colour is discharged. The pro-

⁴⁶ A richly coloured specimen of rose-quartz exhibited in the British Museum collection of minerals has been exposed to light since the year 1799.

⁴⁷ *Amer. J. Sci.*, 1923, [v], 5, 314; 1923, 6, 247; 1924, 8, 509; *Proc. Colorado Sci. Soc.*, 1923, 11, 399; *A.*, ii, 561.

perties are again restored by exposing the calcite to radium, and the material then acquires a yellow colour. Some colourless and previously unresponsive calcites when exposed to radium acquire a yellow colour and become responsive. Detailed chemical analyses were made on large amounts of material (500 grams or even 25 lb.). A strongly phosphorescent, yellow calcite from Joplin contained, in addition to CaCO_3 , about 99.80%: cerium earths 0.019, yttrium earths, 0.013, MgO 0.113, FeO 0.046, MnO 0.045, ZnO 0.014%. The purple Joplin calcite gave: cerium earths 0.0397, yttrium earths 0.0149, MgO 0.0949, Al_2O_3 0.0076, FeO 0.0148, MnO 0.0477, ZnO 0.0048, CuO 0.0090%. The difference in colour cannot be explained by these impurities in the calcite. It has, however, been noticed that the purple calcite alone shows the absorption-spectrum of neodymium, and the suggestion has been made that this is the cause of the purple colour, though there is no direct evidence to support this view. A curious feature was noticed accidentally with a colourless calcite from Ingleside, Colorado. This is sometimes phosphorescent after exposure to sunlight, but only after it has been washed on the surface with dilute hydrochloric acid.⁴⁸

A change in colour due to oxidation of ferrous iron has been observed by A. Johnsen.⁴⁹ Pale yellow to green crystals of sphene from the Alps when heated to redness in air for half an hour become deep reddish-brown, and they then show a different pleochroism and a slight difference in the optic axial angle. When again heated in hydrogen, the original colour is very nearly restored. Material that contained before heating FeO 0.48, Fe_2O_3 0.04%, gave after heating in air FeO 0.40, Fe_2O_3 0.13%, and after subsequent heating in hydrogen FeO 0.52, Fe_2O_3 0.03%. These changes are taken to indicate that there has been a diffusion of material in the solid.

A somewhat similar case is shown by the mineral chlorophæite, though here the change in colour due to oxidation takes place spontaneously on exposure to air. This mineral, which occurs as patches in dolerite near Edinburgh, is pale olive-green with glassy lustre on freshly fractured surfaces. On exposure, the colour changes to dark green in about fifteen minutes, and after ninety minutes it is black with pitchy lustre. It was found that this change takes place also in the dark when the mineral is exposed to air; but not in an atmosphere of carbon dioxide, even on exposure to bright sunlight. The change is therefore due to oxidation, and not to the action of light. The change from pale green to black can be induced artificially by heating a fragment of the mineral in the oxidising part of a Bunsen-

⁴⁸ *Amer. J. Sci.*, 1924, [v], 8, 509; *A.*, ii, 89.

⁴⁹ *Jahrb. Min. Beil.-Bd.*, 1923, 48, 136.

flame. Analysis of the fresh mineral shows the presence of Fe_2O_3 12.37, FeO 9.18%.⁵⁰

A fugitive colour in sodalite is described from Dungannon in Ontario.⁵¹ A rock, consisting of nepheline, cancrinite, and calcite, showed on freshly fractured surfaces bright pink spots, but in direct sunlight these vanished in ten to thirty seconds. When the specimens are placed in the dark, the colour gradually returns, though not to the same brilliancy. The material of the pink areas was identified as sodalite, but the analysis shows no constituent, beyond a trace of manganese, to account for the colour. This colour change is evidently due to the action of light, and no further explanation can be offered. It was first noticed a century ago in sodalite from Greenland,⁵² and later in sodalite from India and in hackmanite from Russian Lapland.

The action of radium radiations on the colour of minerals has been studied by many workers, and a good account has recently been given by S. C. Lind and D. C. Bardwell.⁵³ The colour produced by exposure to radium chloride or bromide is afterwards dispelled by heat or by exposure to sunlight. The most marked effects are given by fluorite and kunzite. Fluorite of all colours becomes blue in 1—3 days; the material when afterwards heated to 70° gives a blue luminescence, and at 180° the colour is discharged. Kunzite, the lilac-coloured variety of spodumene, becomes first colourless and then emerald-green; and is afterwards very brightly thermoluminescent. Diamond becomes green only when exposed to α -radiation (not β - and γ -radiation through glass); this colour is apparently light-permanent, but is dispelled at 450° . A theory to account for these changes assumes that certain groups of electrons are displaced and their vibration frequencies modified.

New Minerals.

A list of 211 new mineral names (not necessarily new minerals) covering the period 1922—1925, but including also a few earlier names that had remained buried in the scattered literature, has recently appeared.⁵⁴ A selection of these not mentioned in previous Reports is given below. A further crop of radioactive minerals from the deposits of uranium ore in the Katanga district of the

⁵⁰ R. Campbell and J. W. Lunn, *Min. Mag.*, 1925, **20**, 435; *A.*, ii, 1093.

⁵¹ T. L. Walker and A. L. Parsons, *Univ. Toronto Studies, Geol. Ser.*, 1925, No. 20, 5.

⁵² F. Mohs, "Treatise on Mineralogy," translated by W. Haidinger, 1825, **2**, 227.

⁵³ *J. Franklin Inst.*, 1923, **196**, 375, 521; *Amer. Min.*, 1923, **8**, 171, 201; 1924, **9**, 35.

⁵⁴ L. J. Spencer, "Tenth list of new mineral names; with an index of authors." *Min. Mag.*, 1925, **20**, 444.

Belgian Congo includes the new names: droogmansite,⁵⁵ dumontite,⁵⁶ fourmarierite, and sklodowskite.⁵⁷

Some of these names are rather uncouth and they do not seem to be well chosen for international use.⁵⁸ The international aspect of Science is of prime importance. An original paper is written in the language of one country, but it is more widely read in the sum of other countries.

A system of Latin binomials (as in botany and zoology) was in use a century ago for minerals, but this has long since been given up. Another method that has been tried without success is that of using purely chemical names. This is favoured by Groth in his "Chemische Krystallographie"; for example, he substitutes for hannayite the name Tetrahydrogendiammoniumtrimagnesiumtetraorthophosphat-Oktohydrat. But this does not completely define the mineral hannayite—there may be others of the same composition. Further, future analyses of hannayite may prove this composition to be incorrect—to the confusion of indexers. For such minerals as tourmaline even Groth does not attempt a chemical name. The system now in vogue, in spite of its confusion and faults, is the best yet devised. It certainly is a convenience to use such names as diamond and graphite for the crystalline modifications of carbon found in nature; and calcite and aragonite for those of calcium carbonate.

Afwillite,⁵⁹ hydrated calcium silicate, $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$, or $2\text{H}_2\text{CaSiO}_4 \cdot \text{Ca}(\text{OH})_2$, found as a single, columnar aggregate of clear, colourless crystals in the Dutoitspan diamond mine at Kimberley, South Africa. The crystals are monoclinic and the mineral is quite distinct from the several hydrated calcium silicates previously known. It has an alkaline reaction and is slowly decomposed by water.

Bardolite,⁶⁰ a dark-green, chlorite-like mineral with the empirical formula $\text{K}_2\text{O} \cdot 5\text{MgO} \cdot \text{FeO} \cdot 2\text{FeO}_3 \cdot \text{Al}_2\text{O}_3 \cdot 12\text{SiO}_2 \cdot 21\text{H}_2\text{O}$, intermediate between biotite and chlorite in composition. It is of interest because of its occurrence as a primary constituent in an igneous rock, namely in diabase at Bardo in central Poland.

⁵⁵ H. Buttgenbach, "Minéralogie du Congo Belge." *Mém. Soc. R. Sci. Liège*, 1925, [iii], 13.

⁵⁶ A. Schoep, *Compt. rend.*, 1924, 179, 693; *A.*, ii, 64; *Bull. Soc. franç. Min.*, 1925, 48, 77.

⁵⁷ A. Schoep, *Compt. rend.*, 1924, 179, 413; *Bull. Soc. franç. Min.*, 1924, 47, 162; *Bull. Soc. chim. Belg.*, 1924, 33, 562; *A.*, 1924, ii, 868; 1925, ii, 235.

⁵⁸ L. J. Spencer, "International agreement in mineralogical and crystallographical nomenclature." *Min. Mag.*, 1925, 20, 353.

⁵⁹ J. Parry and F. E. Wright, *Min. Mag.*, 1925, 20, 277; *A.*, ii, 429.

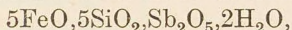
⁶⁰ J. Morozewicz, *Bull. Soc. franç. Min.*, 1924, 47, 49; *Spraw. Polsk. Inst. Geol.*, 1924, 2, 217; 1925, 3, 1.

Benjaminite,⁶¹ sulphobismuthite of lead, silver, and copper, $\text{Pb}_2(\text{Ag,Cu})_2\text{Bi}_4\text{S}_9$, belonging to the klaprotholite group, and found as grey masses in white quartz from Nevada.

Bromellite,⁶² beryllium oxide, BeO , found as small, white, hexagonal prisms in the iron mines at Långban in Sweden. It is very hard, about 9 on the scale. X-Ray analysis shows the crystal-structure to be of the zinc oxide type.

Cannizzarite,⁶³ a sulphobismuthite of lead, $\text{PbS}, 2\text{Bi}_2\text{S}_3$, of recent formation as a sublimate in fumaroles on Vulcano, Lipari Islands. The acicular crystals appear to be orthorhombic.

Chapmanite,⁶⁴ hydrated ferrous silico-antimonate,



occurring as an olive-green, pulverulent material (probably orthorhombic) intermixed with native silver in the Keeley mine, South Lorrain, Ontario.

Foshagite,⁶⁵ hydrated calcium silicate, $5\text{CaO}, 3\text{SiO}_2, 3\text{H}_2\text{O}$ or $\text{H}_2\text{Ca}_5(\text{SiO}_4)_3, 2\text{H}_2\text{O}$, as a white fibrous (orthorhombic) mineral filling veins in idocrase at Crestmore, California.

Fourmarierite, a hydrated uranium lead mineral occurring as minute, red, orthorhombic crystals intimately associated with kasolite, curite, and torbernite in the oxidised uranium ore of Kasolo, Katanga, Belgian Congo. H. Buttgenbach,⁶⁶ by whom the name was given, found also some silica, but this may belong to the associated kasolite. Analyses by J. Mélon⁶⁷ on material separated as far as possible from other minerals suggested the formula $\text{PbO}, 5\text{UO}_3, 10\text{H}_2\text{O}$; while one by A. Schoep⁶⁸ gave $\text{PbO}, 4\text{UO}_3, 5\text{H}_2\text{O}$, which, written in the form $(\text{UO}_2, \text{Pb})\text{O}, \text{H}_2\text{O}$, suggests a relation to becquerelite and schoepite.

Chlorophoenicite,⁶⁹ basic arsenate of manganese and zinc with small amounts of calcium, magnesium, and iron, with the highly basic formula $\text{R}_3\text{As}_2\text{O}_8, 7\text{R}(\text{OH})_2$. It is found at Franklin Furnace,

⁶¹ E. V. Shannon, *Proc. U.S. Nat. Museum*, 1924, **65**, art. 24; *A.*, 1924, ii, 560. For other sulphobismuthites of lead see Cannizzarite and Goongarrite below; still others have been described by K. Johansson, *Arkiv Kemi, Min. Geol.*, 1924, **9**, no. 8.

⁶² G. Aminoff, *Z. Krist.*, 1925, **62**, 113.

⁶³ F. Zambonini, O. de Fiore, and G. Carobbi, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1925, [iii], **31**, 24; *A.*, ii, 709.

⁶⁴ T. L. Walker, *Univ. Toronto Studies, Geol. Ser.*, 1924, No. 17, 5.

⁶⁵ A. S. Eakle, *Amer. Min.*, 1925, **10**, 97.

⁶⁶ *Ann. Soc. Géol. Belg. (Publ. Congo Belge)*, 1924, **47** (for 1923-4), c 41.

⁶⁷ *Ann. Soc. Géol. Belg. (Bull.)*, 1925, **47**, B 200.

⁶⁸ *Bull. Soc. franç. Min.*, 1924, **47**, 157; *Bull. Soc. chim. Belg.*, 1924, **33**, 558; *A.*, 1925, ii, 236.

⁶⁹ W. F. Foshag and R. B. Gage, *J. Washington Acad. Sci.*, 1924, **14**, 362; *A.*, 1924, ii, 773.

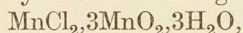
New Jersey, as small, monoclinic prisms, which are pale green by daylight and pale purplish-red in artificial light (hence the name).

Elatolite,⁷⁰ a form of calcium carbonate believed to represent the high-temperature α -form stable above 970°. It is represented by cavities with the form of fir-trees (έλάρη) in the nepheline-syenites of the Kola peninsula in Russian Lapland. The dendritic crystals that have been leached out of these cavities were evidently an original constituent of the igneous rock.

Ellsworthite,⁷¹ hydrated metatitano-niobate of uranium (UO_3 18.5%), calcium, and iron, $\text{RO} \cdot \text{Nb}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, occurring as yellow or brown, optically-isotropic masses in pegmatite at Hybla, Ontario. In its degree of hydration it is intermediate between hatchettolite and ampingabeite.

Goongarrite,⁷² a sulphobismuthite of lead, $4\text{PbS} \cdot \text{Bi}_2\text{S}_3$, occurring as fibrous to platy (monoclinic?) masses in a gold-quartz vein near Lake Goongarrie, Western Australia.

Kempite,⁷³ hydrated oxychloride of manganese,



as small, emerald-green, orthorhombic crystals in manganese ore from California.

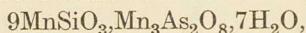
Kochite,⁷⁴ hydrated aluminium silicate, $2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 5\text{H}_2\text{O}$, as a granular aggregate of minute, cubic crystals at Kochi-mura, Japan.

Manganolangbeinite,⁷⁵ manganese and potassium sulphate, $2\text{MnSO}_4 \cdot \text{K}_2\text{SO}_4$, as minute, pale-rose tetrahedra from Vesuvius. It is analogous to the cubic double salt langbeinite, $[\text{2MgSO}_4 \cdot \text{K}_2\text{SO}_4]$.

Mullite, orthorhombic, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (see p. 269).

Ramsayite,⁷⁶ sodium titanosilicate, $\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 2\text{TiO}_2$, occurring as brown, orthorhombic crystals resembling sphene in nepheline-syenite-pegmatite in the Kola peninsula, Russian Lapland.

Schallerite,⁷⁷ hydrated arseno-silicate of manganese,



as pale-brown masses filling veinlets in zinc ore at Franklin Furnace, New Jersey. It has a pearly basal cleavage and is optically uniaxial, and is analogous to friedelite $[\text{9MnSiO}_3 \cdot \text{MnCl}_2 \cdot 7\text{H}_2\text{O}]$.

⁷⁰ A. E. Fersman, *C. R. Acad. Sci. Russie*, 1922, 59; *Bull. Acad. Sci. Russie*, 1923, [vi], 17, 251.

⁷¹ T. L. Walker and A. L. Parsons, *Univ. Toronto Studies, Geol. Ser.*, 1923, No. 16, 13.

⁷² E. S. Simpson, *J. Roy. Soc. Western Australia*, 1924, 20, 65.

⁷³ A. F. Rogers, *Amer. J. Sci.*, 1924, [v], 8, 145; *A.*, 1924, ii, 693.

⁷⁴ S. Kôzu, K. Seto, and K. Kinoshita, *J. Geol. Soc. Tokyo*, 1922, 29, 1, 148; *Sci. Rep. Tôhoku Univ.*, 1924, [iii], 2, 1.

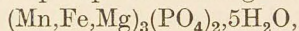
⁷⁵ F. Zambonini and G. Carobbi, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1924, [iii], 30, 123; *A.*, 1924, ii, 867; *Gazzetta*, 1925, 55, 414; *A.*, ii, 898.

⁷⁶ A. E. Fersman, *C. R. Acad. Sci. Russie*, 1922, 59; E. E. Kostyleva, *ibid.*, 1923, 55.

⁷⁷ R. B. Gage, E. S. Larsen, and H. E. Vassar, *Amer. Min.*, 1925, 10, 9.

Swedenborgite,⁷⁸ antimonate of aluminium and sodium, $\text{NaAl}_2\text{SbO}_6$, as colourless, hexagonal crystals from Långban, Sweden.

Wenzelite,⁷⁹ hydrated phosphate of manganese, etc.,



as rosettes of pale rose-red, monoclinic crystals from the phosphate-bearing pegmatites at Hagendorf, Bavaria. Similar crystals, also rose-red and monoclinic from the same locality, but with the composition $\text{R}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, have been called *baldaufite*.⁸⁰

New Books.

"A chart showing the chemical relationships in the mineral kingdom" has been prepared by P. C. Putnam (J. Wiley & Sons, New York; Chapman & Hall, London, 1925). This will be found useful to chemists as well as to mineralogists. It gives the answer to such questions as: "How many and what are the minerals containing germanium, and what are their compositions?"; "Does silver occur with oxygen in any mineral?"; or "Do phosphides or silicides occur as minerals?" It serves as an aid to determinative mineralogy and the microchemical analysis of minerals. And, further, gives at a glance a statistical survey of the affinities and the antipathies that hold in the mineral kingdom. The chart is printed on a sheet measuring a yard across and is mounted on linen. Along the edges various chemical elements, acid radicals, etc., are listed, there being 93 and 54 such entries in the two directions. Ruling vertical and horizontal lines, 5022 "boxes" are thus provided, in which practically all known minerals are placed. A mineral of complex composition will of course appear in several "boxes." The minerals are referred to by numbers 1—1632; and alphabetical and numerical indexes are given in the text. It is thus possible to see at a glance what minerals contain, say, both lead and sulphur, lead and uranium, lead and aluminium, etc. The idea is a good one and the chart will serve many useful purposes.

A new edition has appeared of P. Niggli's "Lehrbuch der Mineralogie." The first volume (Borntraeger, Berlin, 1924) is really a treatise on crystallography, but two more volumes dealing with special mineralogy and mineral associations ("Minerocoenology") are to follow. The treatment is fresh, and the book is full of novel and brilliant ideas, giving stimulus to research. H. Buttgenbach's "Les minéraux et les roches," a general and elementary text-book, has reached a third edition (Dunod, Paris; H. Vaillant-Carmanne, Liège, 1924). A fifth edition of the late H. Rosenbusch's well-

⁷⁸ G. Aminoff, *Z. Krist.*, 1924, **60**, 262.

⁷⁹ F. Müllbauer, *ibid.*, 1925, **61**, 333. In the original paper the name is given erroneously as *Wentzelit*, after Pater Hieronymus Wenzel.

⁸⁰ F. Müllbauer, *loc. cit.*, 334.

known "Mikroskopische Physiographie der Mineralien und Gesteine" is in preparation. The first half of vol. I (1921—4) has been revised by E. A. Wülfing and deals with the methods of investigation, involving crystal-optics, separation of minerals, microchemical tests applicable to powdered minerals and to thin sections, etc. The second half by O. Mügge gives a systematic description of the rock-forming minerals. In the first part so far issued (1925) the minerals of the cubic, tetragonal, hexagonal (and trigonal) systems are dealt with.

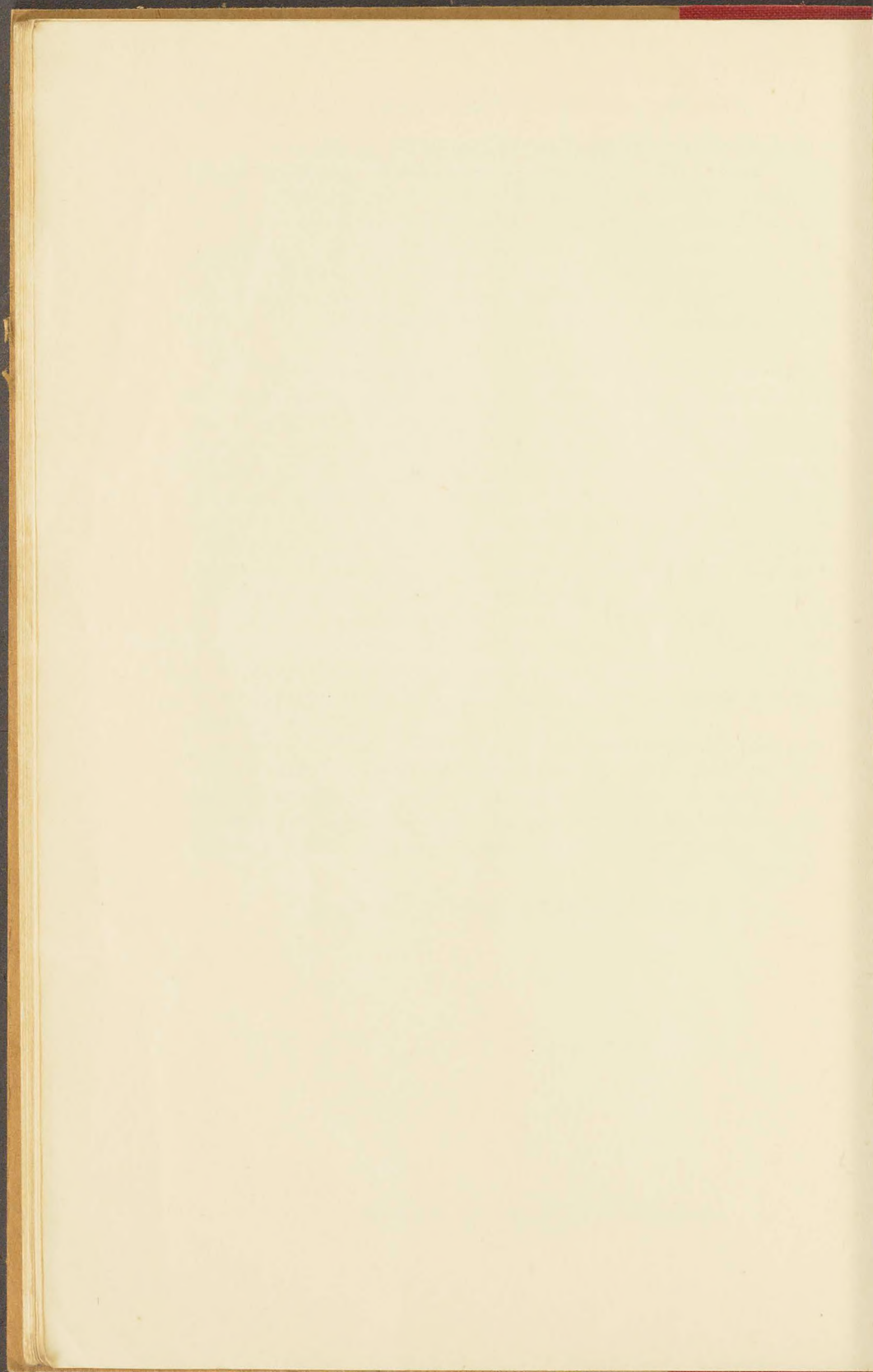
W. Eitel in "Physikalisch-chemische Mineralogie und Petrologie" (T. Steinkopff, Dresden and Leipzig, 1925) gives a condensed report on the work done during the past ten years on the many physical-chemical problems bearing on the formation and equilibrium of minerals and rocks. Numerous references are given to the original literature and there is a long index of authors. The same author in his prize essay "Über die Synthese der Feldspatvertreter" (Akad. Verlagsgesell., Leipzig, 1925) gives a detailed review of the literature on the synthesis of the felspathoid minerals (leucite, nepheline, gehlenite, melilite, sodalite, cancrinite, scapolite, etc.), with a discussion and equilibrium diagrams of the various systems in which they have been obtained artificially by fusion. An account is also given of his own work on carbonate-silicate fusions. The bearing of these experiments on the paragenesis of these minerals in natural rocks is considered.

A pamphlet⁸¹ on "The physical chemistry of igneous rock formation" contains a series of ten papers by various authors, which were presented for general discussion at a joint meeting of the Faraday, Geological, and Mineralogical Societies in London. Contributed remarks and the discussion that arose are also included.

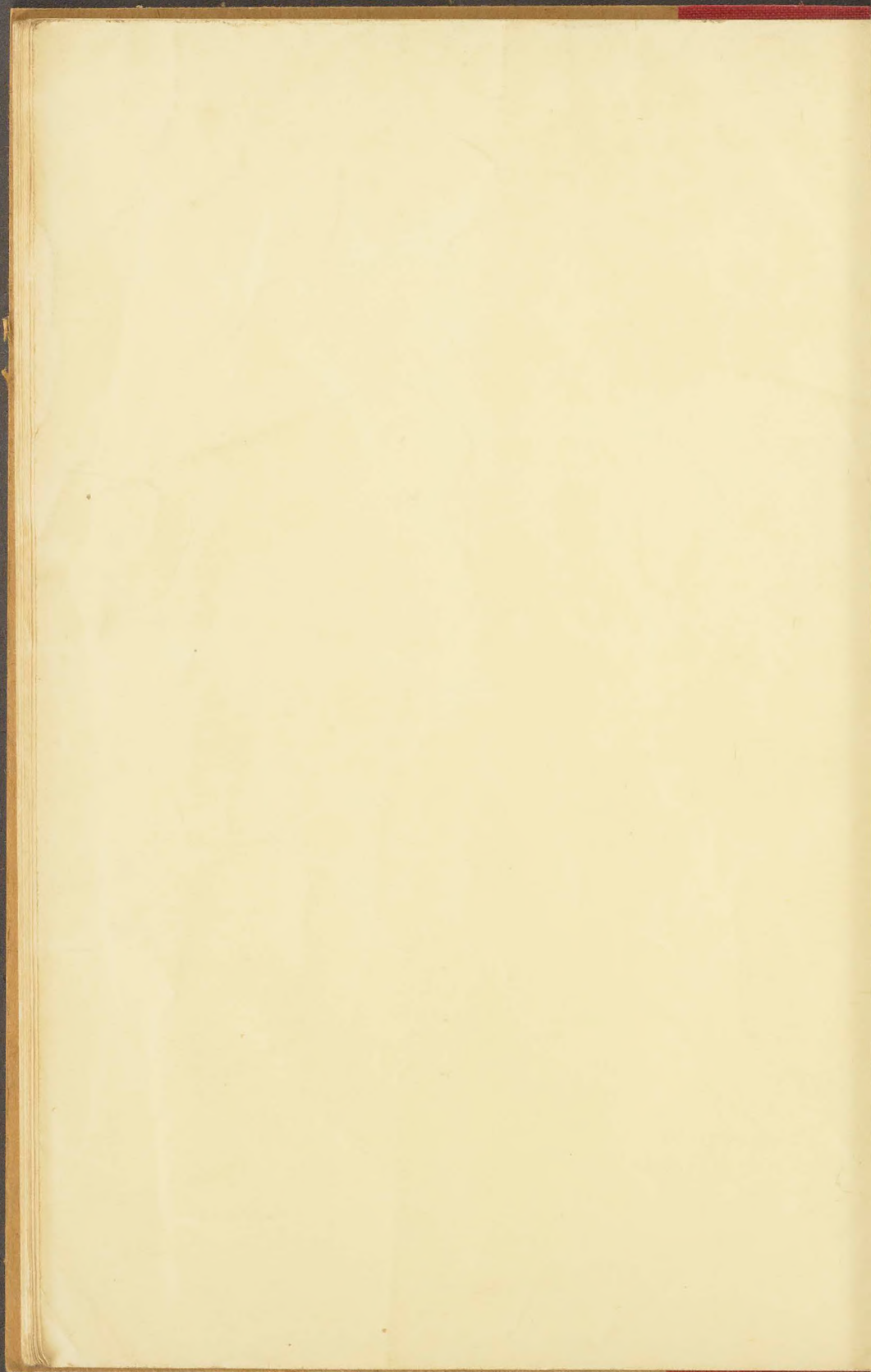
L. J. SPENCER.

⁸¹ Reprinted from *Trans. Faraday Soc.*, 1925, 20, 413.









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MINERALOGICAL CHEMISTRY (1926-7).

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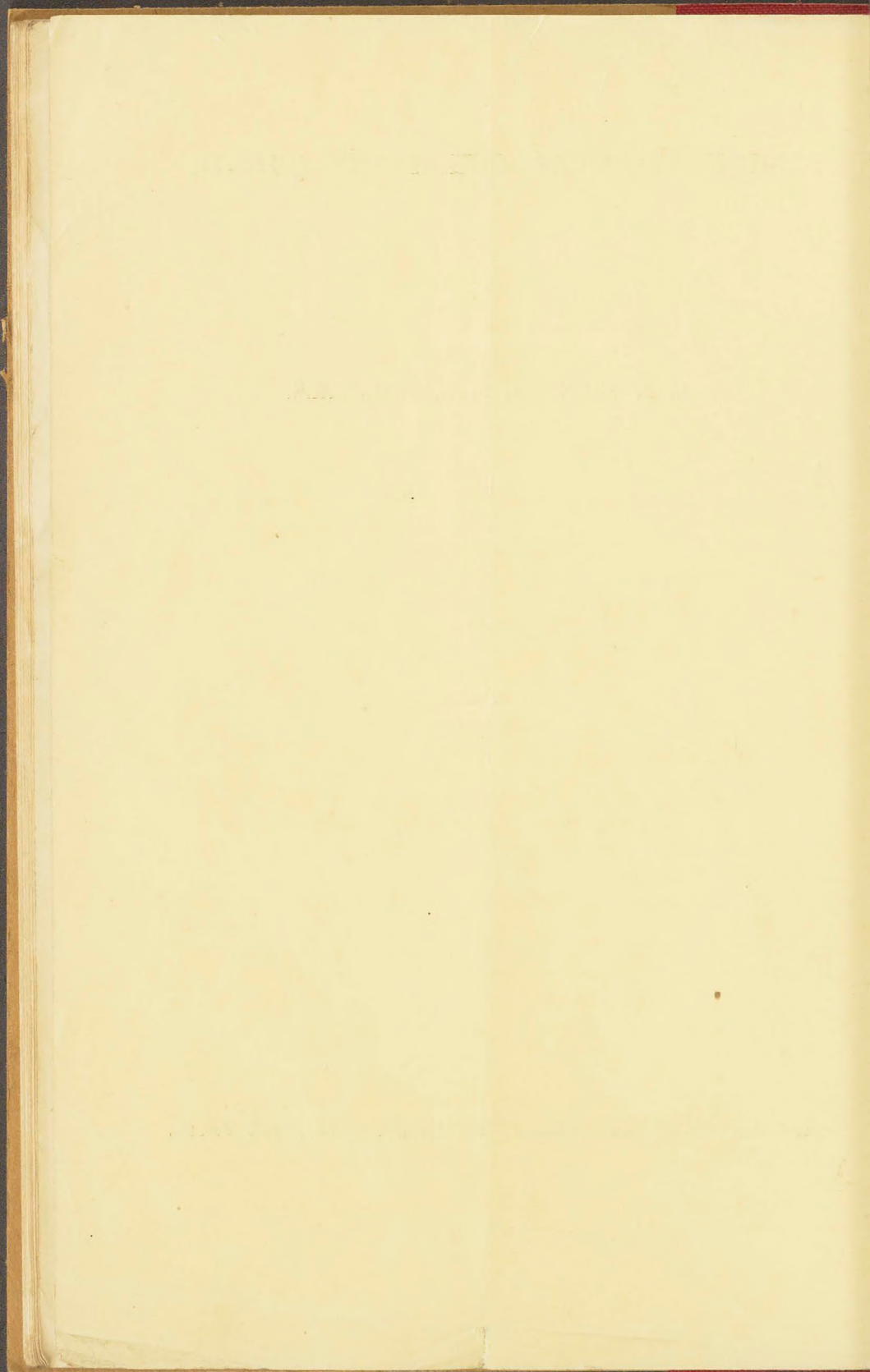
L. J. SPENCER, M.A., Sc.D., F.R.S.

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p. 313

Reprinted from the Annual Reports of the Chemical Society, 1927. Vol. 24.

1928



MINERALOGICAL CHEMISTRY.

GROTH is dead. Paul Heinrich Ritter von Groth (1843—1927) died on December 2nd at the ripe age of 84½ years. He was Professor of Mineralogy in Strassburg during 1872—1883, and since 1883 in Munich, and his laboratory was long the centre of training for students from all parts of the world. In 1877 he founded the *Zeitschrift für Krystallographie und Mineralogie* (carried on since 1921 by Prof. Paul Niggli of Zürich under the title *Zeitschrift für Kristallographie*), in which he obtained the willing co-operation of workers in all countries. As marking the jubilee of that periodical, he gave in vol. 66, only shortly before his death, an interesting review of the work that had been done. His monumental work, "Chemische Krystallographie" (5 vols., 1906—1919), collects together the crystallographic data for some 7350 substances. The extent to which this is now being used by X-ray workers could scarcely have been foreseen even by Groth himself. His well-known text-books "Physikalische Krystallographie" and "Tabellarische Übersicht der Mineralien" each passed through four editions, and only last year he gave an interesting essay on the historical development of the mineralogical sciences.¹ He held a unique position as a leader, and he did more than anyone else in co-ordinating and stabilising crystallographic nomenclature and methods. His name will for ever stand out as a landmark in the history of crystallography.

The deaths² have also to be recorded of two distinguished mineral chemists, who both did valuable work, but on entirely different lines. William Francis Hillebrand (1853—1925), as chemist on the United States Geological Survey, had made many analyses of minerals and rocks, including several rare and new minerals collected by members of the survey in new country. The careful and detailed analytical work for which he was noted led to the recognition of several chemical elements not previously suspected to be present in rocks. In 1888—1892 he made a number of very detailed analyses of uraninite (pitchblende), in which he found a gas. This

¹ "Entwicklungsgeschichte der mineralogischen Wissenschaften," Berlin, 1926.

² L. J. Spencer, "Biographical Notices of Mineralogists Recently Deceased" (third series), *Min. Mag.*, 1927, 21, 229.

gas evidently puzzled him, and he concluded that it was mainly nitrogen. Sir William Ramsay afterwards, in 1895, identified it as helium, and uraninite was the first known terrestrial source of this element. Hillebrand's well-known book "Analysis of Silicate and Carbonate Rocks" was first issued in 1907 as a Bulletin of the United States Geological Survey, and has passed through several editions. Working as a student in Heidelberg under Bunsen he prepared metallic cerium in 1875 and discovered its pyrophoric property, a property which now has an extensive practical application.

Gustav von Tschermak (1836—1927), of Vienna, died on May 4th, at the advanced age of ninety-one years. As distinct from the work of Hillebrand, his work consisted largely in correlating the large amount of data accumulated by analytical chemists and in deducing general principles. The current views of the text-books on the constitution of many of the main groups of silicates are due to him, and were developed in a series of classical papers extending over many years: plagioclase feldspars (1865), pyroxenes and amphiboles (1868), micas (1877), scapolites (1884), chlorites (1890), vermiculites (1891), tourmaline (1899), zeolites (1917—1918). In later years, with the help of his pupils (including his daughter Silvia Hillebrand), he endeavoured to determine the composition of silicic acids isolated from natural silicates. The valuable periodical *Tschermaks Mineralogische und Petrographische Mitteilungen* was commenced by him in 1872, and his well-illustrated "Lehrbuch der Mineralogie" passed through nine editions.

Mineralogical jubilees are now falling due. That of the Mineralogical Society of Great Britain and Ireland (instituted February 3rd, 1876) was celebrated last year,³ and was attended by several distinguished foreign mineralogists. The Société française de Minéralogie was founded on March 21st, 1878, and the fifty volumes of its Bulletin show a record of brilliant work. As noted above, Groth's *Zeitschrift* and Tschermak's *Mitteilungen* were commenced in 1877 and 1872 respectively. The Russian Mineralogical Society dates from a much earlier period (1817), whilst those of Vienna (1901), Germany (1908), America (1919), and Switzerland (1924) are later.

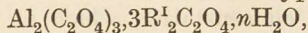
³ Account of the jubilee celebration, *Min. Mag.*, 1926, **21**, 99—148. Reference is there made to the earlier British Mineralogical Society (1799—1806), which consisted of a small group of chemists, including Arthur Aikin, who offered to "examine, free of expense, all specimens of earths or soils, with a view to determining the nature and proportions of their different contents." That society led to the foundation of the Geological Society of London in 1807.

Geochemical Distribution of the Elements.

The series of elaborate papers under this title has been continued by V. M. Goldschmidt,⁴ but in the later numbers the scope of the investigation has been gradually changing—dealing with X-ray determinations of the crystal structure of the rare-earth oxides, the laws of crystal chemistry, etc. It is suggested that elements showing some homœomorphous relation between the crystal structure of their compounds should be found in association in nature. However, work on the original lines has been continued by some of his collaborators. G. Lunde⁵ has examined a variety of minerals and basic igneous rocks from Norwegian localities for traces of platinum metals, finding 0.0000074% Pt in an olivine-rock and in hornblende-gabbro, and 0.000006% in tantalite. The wide distribution of traces of iodine has been further investigated by T. von Fellenberg and G. Lunde.⁶ In meteoric irons and stones, amounts of iodine up to 0.000018% have been detected, together with up to 0.00056% of bromine, the latter especially in the stones. Systematic search for such elements, which are widely distributed although never found in concentrated quantities, is, of course, of some economic importance.

Constitution of Silicates.

A comparative study of mineral silicates with the more tractable organic silicon compounds would no doubt throw some light on the constitution of the former. Some comparisons of this kind were made by the late J. Emerson Reynolds, and by the oxidation of the compound CaSi_2Al_2 (analogous to CaC_2N_2) he synthesised anorthite by an interesting method. A long series of valuable papers by F. S. Kipping and his co-workers on organic derivatives of silicon has appeared in the *Journal* of this Society since 1901. G. N. Ridley,⁷ in a brief outline of some of the present views on the constitution of the silicates, has compared ethyl orthosilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$, with olivine, Mg_2SiO_4 , and ethyl metasilicate, $\text{SiO}(\text{OC}_2\text{H}_5)_2$, with enstatite, MgSiO_3 . On similar lines, W. Wahl has compared aluminosilicates with alumino-oxalates, tracing, it would appear, a close analogy. He had recently proved⁸ that certain alkali aluminium trioxalates of the type



⁴ "Geochemische Verteilungsgesetze der Elemente," Nos. I–VIII, *Videnskapsel. Skrifter, Kristiania* (later *Skrifter Norske Videnskaps-Akad. Oslo*), 1923–7; compare *Ann. Report*, 1923, 20, 262.

⁵ *Z. anorg. Chem.*, 1927, 161, 1; *A.*, 439.

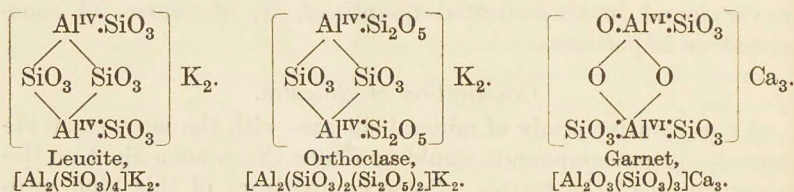
⁶ *Biochem. Z.*, 1926, 175, 162; *A.*, 1926, 1022; 1927, 187, 1; *Beitr. Geophysik*, 1927, 16, 413.

⁷ *Chem. News*, 1925, 131, 305; *A.*, 1925, ii, 1130.

⁸ *Ber.*, 1927, 60, [E], 399; *A.*, 339.

usually regarded as "double salts," can be split up into optically active enantiomorphous isomerides. It therefore becomes necessary to write a co-ordination formula with a central sexavalent ("co-ordination number" 6) aluminium atom, the six C_2O_4 groups being arranged as at the corners of an octahedron to form the tervalent anion.

One of the nine possible types of aluminosilicates is here shown with two aluminium atoms. In some other cases a central quadrivalent aluminium atom forms with two C_2O_4 groups a univalent anion, giving the complex $[\text{C}_2\text{O}_4 \cdot \text{Al}^{\text{IV}} \cdot \text{C}_2\text{O}_4] \text{R}^{\text{I}}$. The aluminosilicates are suggested⁹ to be analogous to these aluminosilicates, and formulæ on the same lines are given for numerous minerals, a "silicyl" group, SiO_3 , or a "bisilicyl" group, Si_2O_5 , taking the place of the oxalato-group. Some of the formulæ, e.g., for the micas, are written to show the polymerisation of the molecule, and these are so large and complex that they are given as text-figures. The following examples may be quoted:



These formulæ suggest an explanation for the breaking down of orthoclase into leucite and silica at a high temperature, for the alteration of felspar to kaolin, of garnet to chlorite, etc. The aluminosilicates being all high-temperature compounds, such formulæ cannot be tested by the methods of stereochemistry, as in the case of organic compounds. They are essentially different from the co-ordination formulæ proposed by J. Jakob.^{9a}

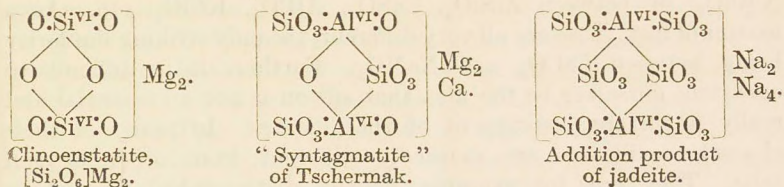
It is further suggested¹⁰ that silicon is not always quadrivalent in the silicates. In the fluosilicates the silicon atom is surrounded by six fluorine atoms and the co-ordination formula is $[\text{Si}^{\text{IV}}\text{F}_6] \text{R}^{\text{I}}_2$. If the fluorine is replaced by oxygen, the compound $[\text{Si}^{\text{IV}}\text{O}_6] \text{R}^{\text{I}}_2$, with the same empirical composition as a metasilicate, is obtained. This is assigned to clinoenstatite, which at a high temperature breaks down into forsterite and silica. A compound similar to this, together with "syntagmatite" and an addition product of

⁹ W. Wahl, *Finska Kemistsamfundets Meddelanden*, 1927, Nos. 1 & 2, 40 pp.; *Z. Krist.*, 1927, **66**, 33, 173.

^{9a} *Helv. Chim. Acta*, 1920, **3**, 669; *A.*, 1920, ii, 754; *Z. Krist.*, 1921 **56**, 295; see *Ann. Report*, 1923, **20**, 266.

¹⁰ W. Wahl, *Ann. Acad. Sci. Fennicae*, Ser. A, 1927, **29**, No. 22.

jadeite, would give molecules with sufficient structural similarity to form isomorphous mixtures, and so explain the presence of aluminium in the amphiboles.



Here there is a replacement of silicon atoms with a co-ordination number of 6 by aluminium atoms also with a co-ordination number of 6. Such a replacement had indeed been suggested for the aluminous amphiboles by P. A. von Bonsdorff in 1821, but this was acceptable only before the current ideas of valency had developed, and these, it seems, must now be modified.

An interesting attempt to elucidate the constitution of the silicates has been made by W. L. Bragg,¹¹ who has attacked the problem from an entirely new point of view. From the results arrived at by the determination of crystal structures by X-ray methods, it is suggested that the structure of silicates is governed by the arrangement of the oxygen atoms. These are assumed to be the largest of all the atoms that enter into the composition of the silicates, and the diameter assigned to them is 2.7 Å. A symmetrical arrangement of such atoms, according to either the cubic or the hexagonal plan of closest packing, is supposed to form the foundation of most silicate structures. The smaller atoms of silicon and of the constituent metals merely fall into the interspaces between the oxygen atoms. In most cases it appears that the silicon atoms lie at the centre of a tetrahedral group of four oxygen atoms, as in the building unit assigned to β-quartz¹² and tridymite.¹³ In determining the structure by X-ray methods of any particular mineral, an attempt is made to locate the precise position of each atom. The relative positions of the several atoms will then give some idea of the chemical constitution.

In 1920 W. L. Bragg,¹⁴ in a series of calculated atomic diameters, gave that of oxygen (1.30 Å.) as the smallest of all the elements. To be told now that it is the largest of all is somewhat disconcerting. If oxygen is to play the governing part in the structure of the silicates,

¹¹ *Proc. Roy. Soc.*, 1927, [A], 114, 450; A., 501; *Proc. Roy. Inst.*, 1927, 25, 302.

¹² (Sir) W. H. Bragg and R. E. Gibbs, *Proc. Roy. Soc.*, 1925, [A], 109, 405; A., 1926, 13.

¹³ R. E. Gibbs, *ibid.*, 1926, [A], 113, 351; A., 1927, 10.

¹⁴ *Ann. Report*, 1920, 17, 201.

it should presumably also do so in the many other oxygen salts; and we might consequently argue that there would be only minor differences in structure between CaSiO_3 , CaCO_3 , CaSO_3 , NaNO_3 , and NaClO_3 , or between ZrSiO_4 , CaSO_4 , AlPO_4 , KClO_4 , etc. As a matter of fact, these are all very different, the only striking similarity being between CaCO_3 and NaNO_3 . Further, it is difficult to accustom ourselves to the idea that silicon is not an essential and really important constituent of the silicates. In many of their characters silicates are markedly different from other oxygen salts. They are, for example, usually distinguished by a high degree of hardness,¹⁵ as compared with the relatively soft carbonates, sulphates, etc. The considerable difference in hardness (5 and 7 on Mohs's scale) in two directions on the same face of a crystal of kyanite presents a peculiar problem; and it must not be forgotten that talc is the softest of minerals.

V. M. Goldschmidt,¹⁶ on the other hand, points out similarities in crystal structure between Zn_2SiO_4 (willemite) and Li_2BeF_4 , and between $\text{CaMgSi}_2\text{O}_6$ (diopside) and $\text{NaLiBe}_2\text{F}_6$. These are evidently homœomorphous relations depending on nearness of molecular volume, as pointed out for many similar cases by J. D. Dana in 1850. In the same place V. M. Goldschmidt suggests that diopside is the calcium salt of "diopside" acid, $\text{H}_2\text{MgSi}_2\text{O}_6$, and jadeite the sodium salt of "jadeite" acid, HAlSi_2O_6 . In another direction he argues,¹⁷ from certain similarities in structure between Mg_2SiO_4 (olivine) and K_2SO_4 on the one hand and Al_2BeO_4 (chrysoberyl) on the other, that the first is an orthosilicate. For the metasilicates MgSiO_3 (enstatite) and CaSiO_3 (wollastonite) he finds no other compounds ABX_3 of the same crystal type, and it is suggested that MgSiO_3 is not a metasilicate, but may be $\text{Mg}_2\text{SiO}_4 + \text{SiO}_2$, and that orthoclase, KAlSi_3O_8 , may be $\text{KAlSiO}_4 + 2\text{SiO}_2$.

Crystallographic similarities, based on "comparative external morphology" as shown by the development of zones and crystal faces, are used as a basis of classification by P. Niggli in the second edition of his "*Lehrbuch der Mineralogie*" (vol. 2, 1926). Here we find silicates ranged with a variety of other minerals: *e.g.*, phenacite with cuprite, wollastonite with borax, kaolin with graphite, tourmaline with aragonite, etc. When the imagination is given full play, crystallography appears to open out endless possibilities. By the skilful manipulation of axial ratios and neglecting discrepancies corresponding with angles up to $7\frac{1}{2}^\circ$ (*i.e.*, half the

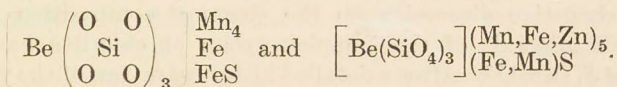
¹⁵ The relation between hardness and crystal structure has been discussed by V. M. Goldschmidt, *Skifter Norske Videnskaps-Akad.*, 1927 (for 1926), No. 8, p. 102.

¹⁶ *Ibid.*, p. 131.

¹⁷ *Ibid.*, 1926, No. 1, p. 110.

difference between 30° and 45°), it is of course possible to demonstrate crystallographically any similarity that may be desired.¹⁸

Helvine, as dark brown tetrahedra associated with fluorite and garnet in pegmatite from a new occurrence in Argentina, has been analysed by W. Fischer,¹⁹ who also gives a full discussion of the various formulæ that have been proposed for this and the closely allied mineral danalite. This analysis [SiO_2 , 32.65; BeO , 12.20; MnO , 30.79; FeO , 14.75; ZnO , 4.89; MgO , 2.24; S , 6.01; total (less O for S), 100.54], in showing the presence of some zinc, indicates a transition from helvine to danalite. When ignited in air the mineral gains 3.18% in weight, and water then extracts iron and manganese sulphates. The formula of helvine was formerly expressed as a double compound of the orthosilicate and monosulphide of the bivalent metals $3(\text{Mn}, \text{Be}, \text{Fe})_2\text{SiO}_4, (\text{Mn}, \text{Be}, \text{Fe})\text{S}$. Since, however, $\text{Be} : (\text{Mn}, \text{Fe})$ is in the constant ratio 3 : 4, the formula is better written as $3(\text{Mn}, \text{Fe})\text{BeSiO}_4, (\text{Mn}, \text{Fe})\text{S}$ or $(\text{Mn}, \text{Fe})_4\text{Be}_3(\text{SiO}_4)_3\text{S}$, representing an isomorphous mixture of $3\text{MnBeSiO}_4, \text{MnS}$ and $3\text{FeBeSiO}_4, \text{FeS}$. This formula was written by Brögger and Bäckström (1890) in the form $(\text{Mn}, \text{Fe})_2(\text{Mn}_2\text{S})^{\text{II}}\text{Be}_3(\text{SiO}_4)_3$ in order to show a relation to the garnet group $\text{R}^{\text{II}}_3\text{R}^{\text{III}}_2(\text{SiO}_4)_3$, where Be_3 takes the place of Al_3 , etc. J. Jakob (1920) gave a co-ordination formula, which was modified by W. Fischer, the two being, respectively,



But, as pointed out by V. M. Goldschmidt,²⁰ this formula corresponds with the ratios $1\text{Be} : 6(\text{Mn}, \text{Fe}) : 3\text{Si} : 12\text{O} : 1\text{S}$, whilst the analyses give $\text{Be}_3(\text{Mn}, \text{Fe})_4\text{Si}_3\text{O}_{12}\text{S}$. X-Ray powder photographs of helvine²¹ are very similar to those given by sodalite, and the unit cubes of edges 8.19 and 8.85 Å. contain two molecules, $\text{Be}_6\text{Mn}_8\text{Si}_6\text{O}_{24}\text{S}_2$ and $\text{Al}_6\text{Na}_8\text{Si}_6\text{O}_{24}\text{Cl}_2$ (sodalite), respectively. C. Gottfried,²² however, finds only one such molecule of helvine in a unit cell of edge 8.52 Å.

Another mineral belonging to the same group and also crystallising as regular tetrahedra is the zunyite from Zuñy mine, Colorado. A new analysis²³ agrees very closely with the earlier analyses of W. F. Hillebrand (1883) and S. L. Penfield (1893), from which the

¹⁸ An example that has always acted personally as a warning in this direction is that given by the comparison of the axial ratios of andorite ($\text{PbAgSb}_3\text{S}_6$), aeschynite, columbite (FeNb_2O_6), and chalcostibite (CuSbS_2) (see *Min. Mag.*, 1897, **11**, 286; 1907, **14**, 320).

¹⁹ *Bol. Acad. Nac. Ciencias, Córdoba*, 1925, **28**, 133; *Centr. Min.*, [A], 1926, 33.

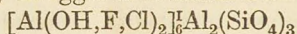
²⁰ *Centr. Min.*, [A], 1926, 148.

²¹ T. Barth, *Norsk Geol. Tidsskr.*, 1926, **9**, 40.

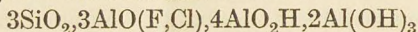
²² *Z. Krist.*, 1927, **65**, 425.

²³ B. Gossner and F. Mussnug, *Centr. Min.*, [A], 1926, 149.

empirical formula $\text{H}_{18}\text{Al}_{16}\text{Si}_6(\text{O},\text{F},\text{Cl})_{45}$ was deduced by Hillebrand. This was modified by Brögger and Bäckström as



to correspond with the garnet formula. B. Gossner and F. Mussnug devised a formula, $\text{SiO}_2, \text{AlF}(\text{OH})_2, 2\text{AlO}_2\text{H}$ or $2\text{SiO}_2, 2\text{AlOF}, 3\text{AlO}_2\text{H}$, in which SiO_2 is partly replaceable by AlO_2H or AlOF (as suggested by the homœomorphism of TiO_2 and MgF_2). Later,²⁴ however, on the ground of X-ray examination of the material analysed, the formula was adjusted so that six molecules



shall be contained in the unit cube of edge 13.92 Å. Surely this is only leading to greater complexity, if not confusion.

B. Gossner has also employed X-ray methods for the purpose of deducing the probable chemical formulæ of some other complex silicates, the formula being readjusted so as to give a whole number of molecules in the unit cell. For example, for the mineral leifite (of O. B. Bøggild, 1915), as calculated from the original formula $\text{Na}_2\text{Al}_2\text{Si}_9\text{O}_{22} \cdot 2\text{NaF}$ ($M = 788.5$), the unit hexagonal cell of dimensions $a = 14.34$, $c = 4.93$ Å. would contain 1.78 molecules. Adoption of a formula $\text{Na}_2\text{Si}_4\text{O}_9, \text{AlOF}$ ($M = 359.5$) gives 3.83 molecules in the unit cell, and this is considered a sufficiently close approximation to 4 to justify the new formula.²⁵

An exhaustive discussion on the chemical composition of the numerous minerals of the complex group of chlorites has been given by J. Orcel.²⁶ After a detailed historical review of the various theories of their constitution, he comes to the conclusion that before these theories can be thoroughly tested more data must be accumulated. He therefore gives a series of new analyses, with density and optical determinations, for nineteen chlorites belonging to various types, including two new types—an aluminous sheridanite and a magnesian thuringite. These and earlier analyses (290 in number) are calculated to the ratios $\text{SiO}_2/\text{R}_2\text{O}_3$, FeO/MgO , $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, and $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, and only empirical formulæ are given. On these ratios is based a new classification of the chlorites: I, Amesite, with $\text{SiO}_2/\text{R}_2\text{O}_3 = s = 1$. II, Corundophyllite group, $s = 1.33$ to 1.66. III, Prochlorite group, $s = 1.66$ to 2.33. IV, Prochlorite-clinochlore group, $s = 2.33$ to 2.66. V, Clinochlore group, $s = 2.66$ to 3.33. VI, Clinochlore-pennine group, $s = 3.33$ to 3.5. VII, Pennine group, $s = 3.5$ to 4.5. VIII, Chlorites poor in alumina, $s > 4.5$. Each of these groups is sub-divided according to the ratios FeO/MgO and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$; but for the ratio $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$

²⁴ B. Gossner, *Jahrb. Min. Beil.-Bd.*, [A], 1926, 55, 319.

²⁵ B. Gossner and F. Mussnug, *Centr. Min.*, [A], 1927, 221.

²⁶ *Bull. Soc. franç. Min.*, 1927, 50, 75; Thèse, Paris, 1927, 380 pp.; 4., 1923, ii, 647; 1924, ii, 621; 1925, ii, 821; A., 1926, 42, 933, 1119.

the chromiferous chlorites are treated in the text as a special group, IX. To fit this classification certain chlorites (aphrosiderite, thuringite, bavalite, daphnite, delessite, diabantite, leuchtenbergite, kotschubeite) have been re-defined, whilst other terms (rumpfte chloropite, protochlorite, dumasite, pseudophite) are regarded as superfluous. Optical data are tabulated with the chemical ratios given above, and it is shown that chlorites of different chemical composition may differ in some cases only slightly optically (*e.g.*, grochanites, clinochlores, and prochlorites). Also dehydration experiments (time-heating curves and pressure of aqueous vapour when the mineral was heated in a vacuum) led to no definite results. Chlorites are usually thought to be secondary minerals, but they may also occur as primary constituents of igneous rocks.

The work of H. S. Washington and H. E. Merwin on the chemical composition and optical and other data of the pyroxenes and amphiboles has been extended to the acmitic pyroxenes,²⁷ and valuable data, all determined on the same sample of material, are recorded. They find that the molecules acmite ($\text{Ac} = \text{Na}_2\text{O}, \text{Fe}_2\text{O}_3, 4\text{SiO}_2$), jadeite ($\text{Jd} = \text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2$), vanadous acmite ($\text{Vac} = \text{Na}_2\text{O}, \text{V}_2\text{O}_3, 4\text{SiO}_2$), diopside ($\text{Di} = \text{CaO}, \text{MgO}, 2\text{SiO}_2$), and hedenbergite ($\text{Hd} = \text{CaO}, \text{FeO}, 2\text{SiO}_2$) may mix in all proportions. For example, an "acmitic diopsidic hedenbergite" is represented by the formula $\text{Ac}10, \text{Jd}6, \text{Di}17, \text{Hd}60, \Delta7$, where Δ represents the sum of such molecules as FeO, SiO_2 ; $\text{Fe}_2\text{O}_3, 3\text{SiO}_2$; $\text{Al}_2\text{O}_3, 3\text{SiO}_2$, etc. Excess of sesquioxides is assumed to be present as $\text{R}_2\text{O}_3, 3\text{SiO}_2$, rather than in the molecules $\text{FeO}, \text{Fe}_2\text{O}_3, 4\text{SiO}_2$ and $\text{FeO}, \text{Al}_2\text{O}_3, 4\text{SiO}_2$, or in solid solution uncombined with silica. Arfvedsonite from Greenland has been the subject of detailed determinations by S. G. Gordon.²⁸ The analyses are interpreted as mixtures of the arfvedsonite molecule ($\text{R}_2\text{O}, 3\text{RO}, 4\text{SiO}_2$), riebeckite molecule ($\text{R}_2\text{O}, \text{R}_2\text{O}_3, 4\text{SiO}_2$), and usually an excess of R_2O_3 , where R_2O is largely Na_2O , and RO and R_2O_3 are chiefly FeO and Fe_2O_3 respectively.

Examination of Minerals by X-Ray Methods.

The crystal structures of a large number of minerals have now been determined by X-ray methods, and a considerable mass of data has been accumulated and in part tabulated.²⁹ Unfortunately,

²⁷ *Amer. Min.*, 1927, **12**, 233.

²⁸ *Proc. Acad. Nat. Sci. Philadelphia*, 1927, **79**, 193.

²⁹ L. J. Spencer in "Tables annuelles de constantes et données numériques," vol. 5 (for 1917—22), p. 1391, Paris, 1926; vol. 6 (for 1923—4), p. 1226, Paris, 1928. R. W. G. Wyckoff in "International Critical Tables," vol. 1, p. 338, Washington, 1926. And in greater detail by P. P. Ewald and C. Hermann, "Strukturbericht, 1913—26," issued as separately-paged supplements in *Z. Krist.*, 1927, **65** et seq.

however, these data have only rarely been correlated with constants determined by other methods on the same sample of material. The majority of original papers give very little idea as to the kind of material that has been used in the experiments, and sometimes it is not clear whether artificially prepared material or a natural mineral has been employed. Due attention does not seem to have been always paid to the careful selection of material, and in a few cases even the identity of the mineral appears to be open to doubt.

Most X-ray workers are content to quote the crystallographic data and density, and even the chemical composition of the material in hand, from P. Groth's "Chemische Krystallographie" (5 vols., 1906—1919). This is a most useful standard work of reference for the crystallographic constants of artificially prepared chemical compounds; but for minerals it is admittedly incomplete, with only a few of the more important references to the original literature, the idea being that the full information was already available in the text-books on mineralogy. For example, under the heading "Berylliumaluminiummetasilicat = $\text{Si}_6\text{O}_{18}\text{Al}_2\text{Be}_3$," Groth gives a very inadequate account of the mineral species beryl. There are several varieties of this mineral. Some contain up to 5% of alkalis (usually cæsium) and most contain up to 2% of water. The text-book formula of beryl can be regarded as only approximate, and it may be doubted if the mineral is really a metasilicate. The density of beryl is given by Groth as 2.6—2.7, but recent determinations show a range from 2.545 to 2.910. The hexagonal crystals, although well developed, sometimes show optical anomalies and a complex intergrowth in sectors. Now, based on this information taken from Groth, a most elaborate structure has been built up for beryl as deduced from the examination of a crystal (or crystals?) by X-ray methods.³⁰ Not the slightest indication is given in the original paper of the kind of material used for this investigation; there is no mention of colour (a useful guide to the varieties of beryl), density, or other characters. "The X-ray measurements lead to a value 2.661 for the density"—but a direct determination would have been more useful.

The same authors³¹ have also, on data quoted from Groth, deduced structures to explain the morphotropic relations of the humite group of minerals. This group has frequently been quoted as a classical example of a morphotropic series. These morphotropic relations are based on the chemical formulæ of Penfield and Howe (1894), which have never been confirmed; and recently they

³⁰ W. L. Bragg and J. West, *Proc. Roy. Soc.*, 1926, [4], 111, 691; *A.*, 1926, 889.

³¹ *Idem, ibid.*, 1927, [4], 114, 450; *A.*, 501.

have been called into question by G. Cesàro,³² who has deduced other formulæ from the original analyses. Further, H. Sjögren's "prolectite" (1895), supposed to be an end member of this series, has been proved to have no existence.³³ The three minerals chondrodite, humite, and clinohumite are not easy of determination and distinction, and it would not appear that the X-ray method affords a practical test.

It is evident that in the examination of minerals exclusively by a single method, such as the X-ray method, a too narrow view is being taken. The same undue importance is often also attached to optical methods in mineralogy. The only papers on minerals in which the materials have been completely examined by all available methods, including X-ray methods, are those by G. Aminoff. For the minerals bromellite,³⁴ magnetoplumbite,³⁵ swedenborgite,³⁶ and trimerite,³⁷ the crystallographic constants, crystal structure, optical data, density, chemical composition, etc., have all been determined on the same sample of material. The history, origin, and paragenesis of the minerals are concisely stated, and the main facts and data are clearly set out, for the benefit of the reader or recorder, without being confused with a mass of more or less irrelevant speculation. Further, the papers are presented once for all in a completed and finished form. There are no preliminary notices, reprints with minor modifications and corrections, and translations in other journals. This simplifies the literature and the work of the bibliographer. These excellent papers may well be taken as a pattern.

Several minerals of the pyroxene group have been examined and compared by the X-ray powder method;³⁸ and here in several cases the work was done on material that had been previously completely determined chemically and optically by the same authors. These minerals give patterns of four main types: (1) Diopside (including hedenbergite, acmite, jadeite, augite); (2) Enstatite (and hypersthene); (3) Wollastonite (and bustamite, pectolite, schizolite); (4) Rhodonite (and calcium-rich rhodonite). Some others (clinoenstatite, spodumene, alamosite, pyroxmangite, sobralite, babingtonite) give other types of pattern. It was found that the replacement of MgO by FeO produces practically no change

³² *Bull. Acad. roy. Belg.*, 1926, **12**, 350; *A.*, 1927, 336.

³³ P. Geijer, *Geol. Förr. Förh.*, 1926, **48**, 86.

³⁴ *Z. Krist.*, 1925, **62**, 113; *Ann. Report*, 1925, **22**, 277.

³⁵ *Geol. Förr. Förh.*, 1925, **47**, 283.

³⁶ *Ibid.*, 1926, **48**, 19.

³⁷ *Z. Krist.*, 1924, **60**, 262; *Ann. Report*, 1925, **22**, 279.

³⁸ R. W. G. Wyckoff, H. E. Merwin, and H. S. Washington, *Amer. J. Sci.*, 1925 [v], **10**, 383; *A.*, 1925, ii, 1126.

in the structure; MnO has a slightly greater volume, and CaO an appreciably greater volume. In augite the excess of Al_2O_3 and Fe_2O_3 has no appreciable effect.

The unit-cell dimensions of the isomorphous members of the garnet group have been determined by G. Menzer³⁹ and also by C. H. Stockwell.⁴⁰ The latter has determined for 40 garnets the refractive index, specific gravity, and the edge of the unit cube (by the X-ray powder method). In only two cases, however, were the determinations made on analysed material; but with the aid of the previous work of W. E. Ford (1915) on the refractive index and specific gravity of the garnets, a correlation was obtained with the chemical composition. Plotting refractive index against specific gravity, Ford found that the garnets fall into two series (almandine-pyrope-spessartine and grossular-andradite), and this is emphasised by plots of the cell dimensions against either the refractive index or the specific gravity. From these data (with, in some few cases, a supplementary qualitative test for manganese), Stockwell was able to determine the nature of a given garnet, and the percentage molecular composition can be calculated. The calculated values for the pure molecules are:

	<i>n.</i>	<i>d.</i>	<i>a.</i>
Pyrope, $\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$	1.705	3.510	11.430 Å.
Almandine $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$	1.830	4.250	11.493
Spessartine, $\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$	1.800	4.180	11.568
Grossular, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$	1.735	3.530	11.840
Andradite, $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$	1.895	3.750	12.040

A good example of how X-ray methods may come to the aid of mineralogical description when ordinary crystallographic methods have failed is given in the case of the new mineral aramayoite,⁴¹ $\text{Ag}(\text{Sb},\text{Bi})\text{S}_2$. Distinctly developed crystals are not available and from the cleavages it could only be concluded that the mineral was perhaps tetragonal. Laue photographs, taken by (Miss) K. Yardley⁴² through the perfect basal cleavage, showed an absence of symmetry, and spectrometer and powder measurements proved the mineral to be triclinic (pseudo-tetragonal). By these means the dimensions of the unit cell and the crystallographic constants were completely determined.

So many workers are now engaged on X-ray research that it often happens that the same mineral has been examined independently several times. For example, the following determinations of the unit orthorhombic cell of baryte (BaSO_4) show a very satisfactory agreement.

³⁹ *Centr. Min.*, [4], 1925, 344; 1926, 343.

⁴⁰ *Amer. Min.*, 1927, 12, 327.

⁴¹ L. J. Spencer, *Min. Mag.*, 1926, 21, 156; *A.*, 1927, 225.

⁴² *Min. Mag.*, 1926, 21, 163; *A.*, 1927, 190.

	<i>a.</i>	<i>b.</i>	<i>c.</i>
S. K. Allison ⁴³	4.449	5.448	7.170 Å.
R. W. James and W. A. Wood ⁴⁴	8.852	5.430	7.132
L. Pauling and P. H. Emmett ⁴⁵	8.846	5.430	7.10
R. W. G. Wyckoff and H. E. Merwin ⁴⁶	8.89	5.45	7.17
F. Rinne, H. Hentschel, and E. Schiebold ⁴⁷ ...	8.88	5.45	7.15
W. Basche and H. Mark ⁴⁸	8.85	5.45	7.14

With one exception, all these authors agree in taking a double value for the *a*-axis, and the axial ratios *a* : *b* : *c*, usually accepted as 0.8152 : 1 : 1.3136, become 1.6304 : 1 : 1.3136. This means that the rarer prism *n*(120) becomes the unit prism instead of the prism parallel to the perfect cleavage, which by crystallographers is naturally taken as a primitive form. The reason for the marked difference in this case is not clear. In this connexion we are reminded of the well-known similarity between the crystal forms of baryte and sulphates, selenates, chromates, perchlorates, and permanganates with the same type of formula, *viz.*, PbSO_4 , BaSeO_4 , BaCrO_4 , KClO_4 , KMnO_4 , etc. F. Rinne ⁴⁹ has referred to these as isotypes of the baryte type, and he points out a remarkable relation between the interfacial angles of the crystals. In baryte the mean of the three angles $(110) : (\bar{1}\bar{1}0) = 78^\circ 22'$, $(011) : (0\bar{1}\bar{1}) = 74^\circ 34'$, $(102) : (\bar{1}02) = 77^\circ 43'$ is $76^\circ 53'$; and in all the other salts the mean of the corresponding angles is, perhaps by a mere coincidence, also $76^\circ 53'$. This angle is near to that ($77^\circ 19'$) of the cubic pentagonal-dodecahedron (540), which in combination with the cube closely resembles the baryte habit. The fact that some of these salts change into a cubic modification at a higher temperature is perhaps related to this approximation to cubic angles. Based on the above similarity, A. E. H. Tutton ⁵⁰ has calculated from the topic axes the dimensions of the unit cells of various perchlorates.

In contrast with the above example of close agreement obtained independently by X-ray workers in different countries, an example may be quoted of lack of agreement. For the indirect determination of density from the structure of mercury telluride (but whether on artificially prepared HgTe or on the mineral coloradoite

⁴³ *Amer. J. Sci.*, 1924, [v], 8, 261; *A.*, 1925, ii, 18.

⁴⁴ *Mem. Manchester Phil. Soc.*, 1925, 69, No. 5; *Proc. Roy. Soc.*, 1925, [A], 109, 598; *A.*, 1926, 13.

⁴⁵ *J. Amer. Chem. Soc.*, 1925, 47, 1026; *A.*, 1925, ii, 485.

⁴⁶ *Amer. J. Sci.*, 1925, [v], 9, 286; *Z. Krist.*, 1925, 61, 452; *A.*, 1925, ii, 485.

⁴⁷ *Z. Krist.*, 1925, 61, 164.

⁴⁸ *Ibid.*, 1926, 64, 1.

⁴⁹ *Centr. Min.*, 1924, 161.

⁵⁰ *Proc. Roy. Soc.*, 1926, [A], 111, 462; *A.*, 1926, 888.

is not in all cases quite clear) the following values have been obtained :

	<i>d.</i>
W. Hartwig ⁵¹	8.025
W. F. de Jong ⁵²	8.20
W. Zachariasen ⁵³	8.42

Microscopic Examination of Opaque Minerals.

The examination under the microscope of polished sections of ore-minerals by reflected light, following the methods of metallography, has been much developed during recent years. This subject, or rather method of investigation, has been called "mineralography" or "mineragraphy" in America and "chalcography" (Chalkographie) ⁵⁴ in Germany. Text-books have been written by J. Murdoch (New York, 1916), W. M. Davy and C. M. Farnham (New York, 1920), H. Schneiderhöhn (Berlin, 1922), and R. W. van der Veen (The Hague, 1925), and a useful outline with detailed bibliography has been given by J. Orceel. ⁵⁵ Various chemical reagents are applied to the polished surfaces for the purpose of distinguishing one mineral from another. More recently, the method has been extended by the use of polarised light, it being possible to distinguish between isotropic and anisotropic crystals and to determine the directions of the principal axes of refraction and of absorption. The method has been extensively applied in America and Germany to the study of ores and ore-deposits. In addition to identifying the various minerals present in the ore, much can be learnt from their mutual relations and order of deposition.

Various obscure and doubtful metallic minerals examined by this method have been proved to be really mixtures, and the complex chemical formulæ that have been applied to them are thus readily explained. The formula of bornite has been usually given as Cu_3FeS_3 ; but the mineral is frequently intergrown with chalcopyrite, chalcocine, etc., and even well-developed crystals often contain a nucleus of chalcopyrite. Recent analyses made on material proved microscopically to be homogeneous have given the formula Cu_5FeS_4 . ⁵⁶ In argentiferous galena it has been shown

⁵¹ *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1926, 79; *A.*, 1926, 664.

⁵² *Z. Krist.*, 1926, 63, 466; *A.*, 1926, 996.

⁵³ *Norsk Geol. Tidsskrift*, 1926, 8, 302; also *Z. physikal. Chem.*, 1926, 124, 277; *A.*, 1927, 96, where the value 8.123 is given.

⁵⁴ The term chalcography has been in use in English since at least the year 1661 for the art of engraving on copper.

⁵⁵ *Bull. Soc. franç. Min.*, 1926, 48 (for 1925), 272—361; *Rev. Mét.*, 1926, 23, 537, 618.

⁵⁶ J. Orceel, *Bull. Soc. franç. Min.*, 1926, 48 (for 1925), 340.

that the silver is present as specks of tetrahedrite or argentite, or sometimes, in richer samples, as veinlets of ruby-silver. The examination of polished sections of the selenium ores from the Harz Mountains has led to the identification of umangite (Cu_3Se_2) in addition to the selenium minerals previously known from this locality. In polarised light the umangite shows a strong pleochroism, from cherry-red to grey.⁵⁷ The complex intergrowths of arsenides and sulpharsenides of cobalt, nickel, and iron occurring at Cobalt in Ontario have also been studied by this method.⁵⁸

The two modifications of silver sulphide, the cubic argentite and the orthorhombic acanthite, were found by H. Schneiderhöhn⁵⁹ in 1922 to be optically anisotropic and both presumably orthorhombic. Crystals of argentite show a complex lamellar structure and are evidently paramorphs after the high-temperature cubic modification, as is the case with leucite. The inversion temperature for silver sulphide is 180° . Similarly, cuprous sulphide is dimorphous as represented by orthorhombic crystals of the mineral chalcosine and by artificially prepared cubic crystals, the latter being stable above 91° . In the copper ores of Tsumeb in South-West Africa, Schneiderhöhn found in 1920 that the chalcosine is of two kinds: (1) a more abundant form with a granular structure and presumably of secondary formation; (2) one showing a complex lamellar structure with an octahedral arrangement, very similar to the structure shown by meteoric irons. The latter he concluded was the primary ore which had crystallised as the cubic modification at a temperature above 91° , and which on cooling passed over into the orthorhombic modification. The presence of "lamellar argentite" or of "lamellar chalcosine" fixes two points (180° and 91°) on the "geological thermometer" in any discussion on the origin of ore-deposits. These conclusions, arrived at by the metallographic method, on the dimorphous relations of the silver and cuprous sulphides, have since been amply confirmed by the X-ray method when the materials were examined at different temperatures.⁶⁰

Forms of Calcium Carbonate.

While "conchite" and "ktypeite" are evidently compact forms of aragonite, the artificially prepared vaterite is doubtless distinct from both calcite and aragonite, and it appears to be identical with the $\mu\text{-CaCO}_3$ of Johnston, Merwin, and Williamson (*Ann. Report*,

⁵⁷ G. Frebold, *Centr. Min.*, [A], 1927, 16, 196; J. Olsacher, *ibid.*, p. 170.

⁵⁸ E. Thomson, *Univ. Toronto Studies, Geol. Ser.*, 1925, No. 20, 54.

⁵⁹ *Amer. Min.*, 1927, 12, 210.

⁶⁰ F. Rinne, *Z. Krist.*, 1924, 60, 299; L. S. Ramsdell, *Amer. Min.*, 1925, 10, 281; R. C. Emmons, C. H. Stockwell, and R. H. B. Jones, *ibid.*, 1926, 11, 326; T. Barth, *Centr. Min.*, [A], 1926, 284.

1917, 14, 241). More recently, Gibson, Wyckoff, and Merwin⁶¹ find by the X-ray powder method that the spherulitic material, to which the name "vaterite" has been applied, includes two forms: "vaterite A" prepared by the method of Johnston, Merwin, and Williamson is spherulitic calcite; whilst "vaterite B" (*i.e.*, the true vaterite), obtained from colloidal calcium carbonate at 5° in the presence of an excess of potassium carbonate, is μ -CaCO₃. The latter was obtained by Johnston, Merwin, and Williamson as hexagonal plates. F. Heide⁶² finds that the gelatinous precipitate given by solutions of *N*/2-potassium carbonate and 2*N*-calcium chloride at 5° changes after 1½–2 hours to minute (3–10 μ) radially-fibrous spherulites of vaterite. Heated at 100° in water, this is transformed into calcite, but the dry material is stable up to 430–440°. X-Ray powder photographs show a structure different from that of both calcite and aragonite. The hexagonal cell of vaterite has dimensions $a = 4.120$, $c = 8.556$ Å., and contains two molecules of CaCO₃; the calculated density is 2.645. After heating at 430–440°, the material shows the lines of calcite in the X-ray photographs.⁶³

At higher temperatures the rhombohedral calcite is the only stable modification, but transformation into α -CaCO₃ at 970° under pressure in an atmosphere of carbon dioxide was recorded by H. E. Boeke in 1912. Such a transition point could, however, not be found by F. H. Smyth and L. H. Adams,⁶⁴ and they placed the melting point of calcite at 1339° under 779,000 mm. pressure. This has an important bearing on the question of the occurrence of primary calcite in igneous rocks, the so-called magmatic calcite, about which there has recently been much discussion. Magmatic carbonate rocks ("carbonatites") were described by W. C. Brøgger (1921) from the Fen district in Norway; and E. Schuster (1919) and R. Brauns (1919) have described calcite-pegmatite and calcite-syenite from the Laacher See district in Rheinland. This has been disputed by N. L. Bowen,⁶⁵ who considers that such occurrences represent secondary replacement of silicates, particularly feldspars, by calcite. When limestone rocks are invaded by igneous magmas, there appears no reason why calcium carbonate should not be incorporated in the mass and melted. There is, for example, abundant evidence of this in the pegmatite veins and nepheline-

⁶¹ *Amer. J. Sci.*, 1925, [v], 10, 325; *A.*, 1925, ii, 1183.

⁶² *Centr. Min.*, 1924, 641.

⁶³ F. Heide, *ibid.*, [A], 1925, 198.

⁶⁴ *J. Amer. Chem. Soc.*, 1923, 45, 1167; *A.*, 1923, ii, 490.

⁶⁵ *Amer. J. Sci.*, 1924, [v], 8, 1; *Centr. Min.*, [A], 1926, 241; *Amer. J. Sci.*, 1926, [v], 12, 499; and replies by R. Brauns, *Centr. Min.*, [A], 1926, 1 and 245.

syenites of Canada. Some authors⁶⁶ have further attempted to prove that such calcite shows peculiarities of structure marking its inversion from α -CaCO₃ as the temperature fell below 970°, this being taken as a point on the "geological thermometer," in the same way that the change from β -quartz to α -quartz⁶⁷ fixes the point 575°. The distinction appears, however, to be based mainly on lamellar twinning and optical anomalies, such as may be produced artificially in calcite by pressure. The name elatolite⁶⁸ has been applied to what is believed to have been α -calcite leached out of tree-like cavities in the nepheline-syenites of the Kola peninsula in Russian Lapland.

The minerals hydroconite, hydrocalcite (trihydrocalcite, penta-hydrocalcite), and lublinitite periodically come to be regarded as doubtful minerals, because when re-examined on museum material they are found to be merely calcite. Hydrated calcium carbonate (CaCO₃.6H₂O) is stable only below 5°, and in nature it is but rarely observed in the winter as a mould-like efflorescence on limestone and chalk. To preserve such a mineral a refrigerator would be required. In addition to the hexahydrate,⁶⁹ crystals of the pentahydrate have also been prepared; whilst a trihydrate, perhaps stable between 17° and 25°, could not be isolated.⁷⁰

Determinative Tables.

E. S. Fedorov's method of crystallo-chemical analysis (*Ann. Report*, 1923, 20, 289), on which great hopes were laid, has not come into general use. The symbols he uses are not generally intelligible, and the introduction to his volume "Das Krystallreich" is so written that from the volume itself it is not possible to understand his method. A. K. Boldyrev, in a pamphlet published by the Russian Academy of Sciences,⁷¹ explains doubtful passages in this introduction and gives supplementary explanations for the instruction of the reader. Boldyrev⁷² has also published

⁶⁶ T. L. Walker and A. L. Parsons, *Univ. Toronto Studies, Geol. Ser.*, 1925, No. 20, 14; J. L. Gillson, *Amer. Min.*, 1927, 12, 357.

⁶⁷ Unfortunately there is here some confusion in nomenclature: α -CaCO₃ or α -calcite is the high-temperature modification, whilst in quartz the high-temperature modification is denoted as β -quartz and the low-temperature modification as α -quartz.

⁶⁸ A. E. Fersman, 1922—3; *Ann. Report*, 1925, 22, 278.

⁶⁹ *Ann. Report*, 1923, 20, 277.

⁷⁰ J. Hume, *J.*, 1925, 127, 1036; *A.*, 1925, ii, 697; J. Hume and B. Topley, *J.*, 1926, 2932; *A.*, 1927, 12.

⁷¹ "Kommentarien zum Werk von E. S. Fedorow: 'Das Krystallreich'" [Russian with German résumé], Leningrad, 1926, 72 pp. [*Min. Mag. (Abstr.)*, 1927, 3, 326].

⁷² *Mém. Soc. Russe Min.*, 1924, 53, 251 [*Min. Mag. (Abstr.)*, 1926, 3, 159].

a criticism of the method in which he points out that there is some difficulty in arriving at the correct complex-symbol. He has therefore suggested and worked out in some detail another method of "crystallo-chemical analysis." This method is based on interfacial angles taken in conjunction with other characters. Some 9000 substances have been entered on catalogue cards and sorted according to the angles in each crystal system. The cards give for each substance: (1) a list of the common crystal forms in the order of their importance, cleavage, twinning, etc.; (2) physical and optical data; (3) the important crystal angles. In the optically uniaxial systems the angles given are those to the basal plane, and in the remaining systems the angles to the axial planes (from which the latitude and longitude, ρ and ϕ , angles of two-circle goniometry can be deduced if wanted). The method is explained in the French résumé, and sample cards are printed in German in the Russian text. The data have been largely compiled from P. Groth's "Chemische Krystallographie." One of the examples given for the orthorhombic system is "orthorhombic tin" ("β-tin"). If the cards had sorted out properly it would have been noticed that this is identical with stannous sulphide.⁷³

Determinative tables or keys of various kinds have long been used in mineralogy. They have been based on obvious external characters, such as lustre, colour, and streak, supplemented by hardness, specific gravity, system of crystallisation, optical characters, etc. In one ingenious device a number of perforated sheets each corresponding with a certain character are laid over a sheet on which are printed the names of minerals until at last the name of the mineral wanted appears in the only opening left. Rule-of-thumb methods of this kind only lead to error, and any table or key must be used with a certain amount of understanding and intelligence. The main use of a table is in suggesting what a given mineral may or may not be, and then some special test must be applied. E. S. Larsen's tables of optical data (*Ann. Report*, 1923, 20, 290) are perhaps the most practical and useful that have yet been devised for determinative purposes. A table of specific gravities may also be a useful aid for the identification of minerals. A recent table⁷⁴ gives a numerical list of 2277 determined values collected from the literature for the period 1910—1927; and an alphabetical list of mineral names gives the minimum and maximum values recorded for each mineral.

A useful table might be compiled from the data given by the unit-cell dimensions (in Ångström units) of crystals as determined

⁷³ Compare *Min. Mag.*, 1921, 19, 113.

⁷⁴ L. J. Spencer, *Min. Mag.*, 1927, 21, 337.

by X-ray methods. In such a table, with a numerical arrangement, there would be a considerable differentiation of the various kinds of materials. The X-ray patterns given by the powder method of various known minerals have already been used by several workers as standards for comparison for the purpose of identifying the minerals present in intimate mixtures (*Ann. Report*, 1923, 20, 282). A reference collection of the X-ray powder patterns of chemically analysed samples of minerals has been commenced in the Department of Geology of the University of Wisconsin.⁷⁵

New Minerals.

A considerable number of "new" minerals have been described more or less completely since the last Report. The following list is limited to those that appear to be distinctive and well established. The ten lists of new mineral names that have been published at the end of each volume of the *Mineralogical Magazine* since 1897 include all names not recorded in Dana's "System of Mineralogy" (6th ed., 1892) and show a total of 1506 names. These are now all collected together in a general index to the set of volumes.⁷⁶

Undoubtedly many more minerals remain to be discovered, although it is of course not to be expected that all known inorganic compounds will be found in the native state. P. N. Chirvinsky,⁷⁷ in a note on the prediction of minerals by mineral synthesis, gives a list of 163 chemical elements and compounds that had been prepared artificially before they were known as minerals. He also gives statistical data of the new minerals described during the past 20 years, and finds that silicates and phosphates predominate.

The suggestive work of the late Baron A. de Schulten might be extended in this connexion. He prepared artificially a number of minerals in a crystallised form and determined the crystallographic and physical constants for the pure compounds. He then proceeded to prepare the analogous compounds in the same isomorphous series. For example, having obtained crystals of artificial monetite, CaHPO_4 , he then prepared the corresponding compounds in which strontium, barium, or lead takes the place of calcium, and arsenic the place of phosphorus. In this series he determined the crystallographic constants and optical data for CaHPO_4 , SrHPO_4 , BaHPO_4 , PbHPO_4 , SrHAsO_4 , and PbHAsO_4 . Crystals of CaHAsO_4 were also obtained but they were too small for measurement. Any of these compounds might be expected to occur in nature, but hitherto

⁷⁵ A. N. Winchell, "Finger Prints of Minerals," *Amer. Min.*, 1927, 12, 261.

⁷⁶ L. J. Spencer, *Min. Mag.*, 1926, General Index to vols. 11—20 (1895—1925).

⁷⁷ P. Tschirwinsky, *Z. Krist.*, 1926, 64, 544.

only monetite has been known. Recently his "arsenical lead monetite" has been found as a mineral and named schultenite (p. 313 below).

Two recently found minerals, not yet completely described, appear to represent new compounds of palladium. One of them, of sparing occurrence in the diamond washings of British Guiana, was determined by the late Sir John Harrison⁷⁸ to be a palladium mercuride with the probable formula PdHg . The small silver-white nuggets and grains have a density up to 15.82, *i.e.*, considerably higher than that of either palladium or mercury. This mineral has since been named potarite, from the Potaro River in British Guiana. A palladium antimonide,⁷⁹ Pd_3Sb , has been found, in association with fine large crystals of sperrylite⁸⁰ (PtAs_2), in the Potgietersrust platinum fields, Transvaal, where minute silver-white grains were detected in pannings of the platinum ore.

*Ammoniojarosite*⁸¹ is one of the few minerals containing ammonium and is interesting in illustrating the wide range of isomorphous replacement in the jarosite group.

Jarosite	$\text{K}_2\text{O}, 3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 6\text{H}_2\text{O}$
Natrojarosite	$\text{Na}_2\text{O}, 3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 6\text{H}_2\text{O}$
Plumbojarosite	$\text{PbO}, 3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 6\text{H}_2\text{O}$
Argentojarosite	$\text{Ag}_2\text{O}, 3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 6\text{H}_2\text{O}$
Ammoniojarosite	$(\text{NH}_4)_2\text{O}, 3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 6\text{H}_2\text{O}$

Ammoniojarosite was found as small ochre-yellow nodules with tschermigite (ammonium alum) in lignitic shale; and, like all the other members of the group, it comes from Utah. Still another member of the same group is probably carphosiderite, $\text{H}_2\text{O}, 3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 6\text{H}_2\text{O}$. Replacing ferric oxide by alumina, another section of this isomorphous group is represented by alunite and natroalunite. Further, the sulphate may be partly or wholly replaced by phosphate, giving several sulphato-phosphates (beudantite, svanbergite, etc.) and phosphates (hamlinite, florencite, etc.), all of which are closely related crystallographically to jarosite and alunite.

Aramayoite,⁸² sulphantimonite and sulphobismuthite of silver, $\text{Ag}(\text{Sb}, \text{Bi})\text{S}_2$, is found in a silver-tin vein in Bolivia as iron-black platy aggregates with brilliant metallic lustre on the perfect basal cleavage. It breaks up into square (or nearly square) plates

⁷⁸ J. B. Harrison and C. L. C. Bourne, *Off. Gazette Brit. Guiana*, Feb. 27, 1925, No. 71; *A.*, 1925, ii, 593.

⁷⁹ H. R. Adam, *J. Chem. Met. Soc. S. Africa*, 1927, 27, 249; *A.*, 851.

⁸⁰ L. J. Spencer, *Min. Mag.*, 1926, 21, 94.

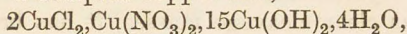
⁸¹ E. V. Shannon, *Amer. Min.*, 1927, 12, 424.

⁸² L. J. Spencer, *Min. Mag.*, 1926, 21, 156; *A.*, 1927, 225; E. Kittl, *Revista Minera de Bolivia*, 1927, 2, 53.

bounded at the sides by fibrous pyramidal cleavages. In the absence of definite crystal faces for goniometric measurement, it appeared to be tetragonal, but as determined by X-ray methods⁸³ it is shown to be triclinic (pseudo-tetragonal), and the crystallographic constants have been completely determined.

Avogadrite, potassium fluoborate, KBF_4 , occurs as minute orthorhombic plates (homœomorphous with baryte, BaSO_4 , KMnO_4 , and KClO_4) in saline sublimations from the floor of the crater of Vesuvius. The detection⁸⁴ spectroscopically of notable amounts of caesium together with potassium in the aqueous extract of these sublimations led to the discovery of the new mineral, and its characters were more completely determined on material recrystallised from this solution.⁸⁵ A comparison of the data so obtained with the physical constants of pure potassium fluoborate and of pure caesium fluoborate suggested that the crystals of avogadrite contained KBF_4 , 90.5%, and CsBF_4 , 9.5%. A later crop of recrystallised material gave data (d 2.498, n_{Na} 1.325) agreeing more closely with those for pure potassium fluoborate.⁸⁶ The refractive index is less than that of water.

Buttgenbachite,⁸⁷ a complex copper salt,



differs from connellite [$2\text{CuCl}_2 \cdot \text{CuSO}_4 \cdot 15\text{Cu}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$] in containing nitrate in place of sulphate. It is found as a fine felt of sky-blue needles with native silver in cavities in cuprite at Likasi, Belgian Congo. The crystals are hexagonal, and buttgenbachite is optically negative, whilst connellite is positive. The two minerals are the end members of an isomorphous series in which mixed crystals occur; previously, W. E. Ford and W. M. Bradley, in 1915, had found 0.72% of N_2O_5 in connellite from Arizona.

Fluoborite,⁸⁸ a fluoborate of magnesium, $3\text{MgO} \cdot \text{B}_2\text{O}_3 + 3\text{Mg}(\text{F},\text{OH})_2$, has been found as colourless hexagonal prisms in an iron mine at Norberg, Sweden.

Ianthinite,⁸⁹ hydrated uranous oxide, $2\text{UO}_2 \cdot 7\text{H}_2\text{O}$ (?), representing an intermediate alteration product of pitchblende at the Kasolo

⁸³ (Miss) K. Yardley, *Min. Mag.*, 1926, 21, 163; *A.*, 1927, 190.

⁸⁴ F. Zambonini and L. Coniglio, *Atti (Rend.) R. Accad. Lincei*, 1926, [vi], 3, 521; *A.*, 1926, 816. ⁸⁵ F. Zambonini, *ibid.*, p. 644; *A.*, 1926, 934.

⁸⁶ G. Carobbi, *ibid.*, 4, 382; *A.*, 1927, 129.

⁸⁷ A. Schoep, *Compt. rend.*, 1925, 181, 421; *Bull. Soc. chim. Belg.*, 1925, 34, 313; *A.*, 1925, ii, 1196; H. Buttgenbach, *Ann. Soc. géol. Belg.*, 1926, 50, Bull. 35; A. Schoep, *ibid.*, 1927, 49 (for 1926), Bull. 308; 1927, 50 (for 1926—7), Bull. 215.

⁸⁸ P. Geijer, *Geol. För. Förh.*, 1926, 48, 84; *Årsbok Sveriges Geol. Unders.*, 1927, 20 (for 1926), No. 4.

⁸⁹ A. Schoep, *Natuurwetensch. Tijds.*, 1926, 7 (for 1925), 97; *ibid.*, 1927, 9, 1; *Ann. Soc. géol. Belg.*, 1927, 49 (for 1926), Bull. 188, 310.

mine, Katanga, Belgian Congo, forms minute orthorhombic crystals with a micaceous cleavage in one direction. The crystals are black with a violet tinge and semi-metallic lustre; the pleochroism is intense—dark violet to colourless. Some of the crystals are bordered by a yellow zone and others are completely changed to a yellow material. A crystal of ianthinite heated at 50° in a drop of water changes from violet to brown and finally to yellow. These yellow alteration products are perhaps becquerelite and schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$), although they differ from these in their optical characters. The refractive indices⁹⁰ of ianthinite are $n_a = 1.674$, $n_\beta = 1.90$, $n_\gamma = 1.92$. A specimen acquired in 1922 for the mineral collection of the British Museum has since been identified as ianthinite. It shows a velvet-like pile of minute needles on pitchblende. When acquired, the colour was purple, but now (1927) it is greenish-yellow; crystals that had been mounted in Canada balsam still retain their original colour and intense pleochroism. The change is evidently due to oxidation in the air of a hydrated uranous oxide to a hydrated uranic oxide.

*Kernite*⁹¹ is hydrated sodium borate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$, containing less water of crystallisation than borax. As large orthorhombic crystals and as clear cleavage masses, it has been found in some quantity in bore-holes in Kern Co., California.

Malladrite,⁹² sodium fluosilicate, Na_2SiF_6 , occurs as minute hexagonal prisms, together with hieratite (K_2SiF_6) in material collected from fumaroles on Vesuvius. The recrystallised material shows regular growths of the cubic potassium salt on the hexagonal sodium salt. Another fluosilicate, cryptohalite $[(\text{NH}_4)_2\text{SiF}_6]$, had been previously observed on Vesuvius.

Schultenite,⁹³ lead hydrogen arsenate, PbHAsO_4 , colourless monoclinic crystals of platy habit, is found on pseudomorphous crusts after mimetite and anglesite at Tsumeb, South-West Africa. The table of angles for the several crystal forms is set out to give the angle from each face to the three axial planes, this method combining the advantages of both the arrangement of interfacial angles in zones and the latitude and longitude angles of two-circle goniometry.⁹⁴

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⁹⁰ V. Billiet, *Natuurwetensch. Tijds.*, 1926, 7 (for 1925), 112; *Bull. Soc. franç. Min.*, 1926, 49, 136.

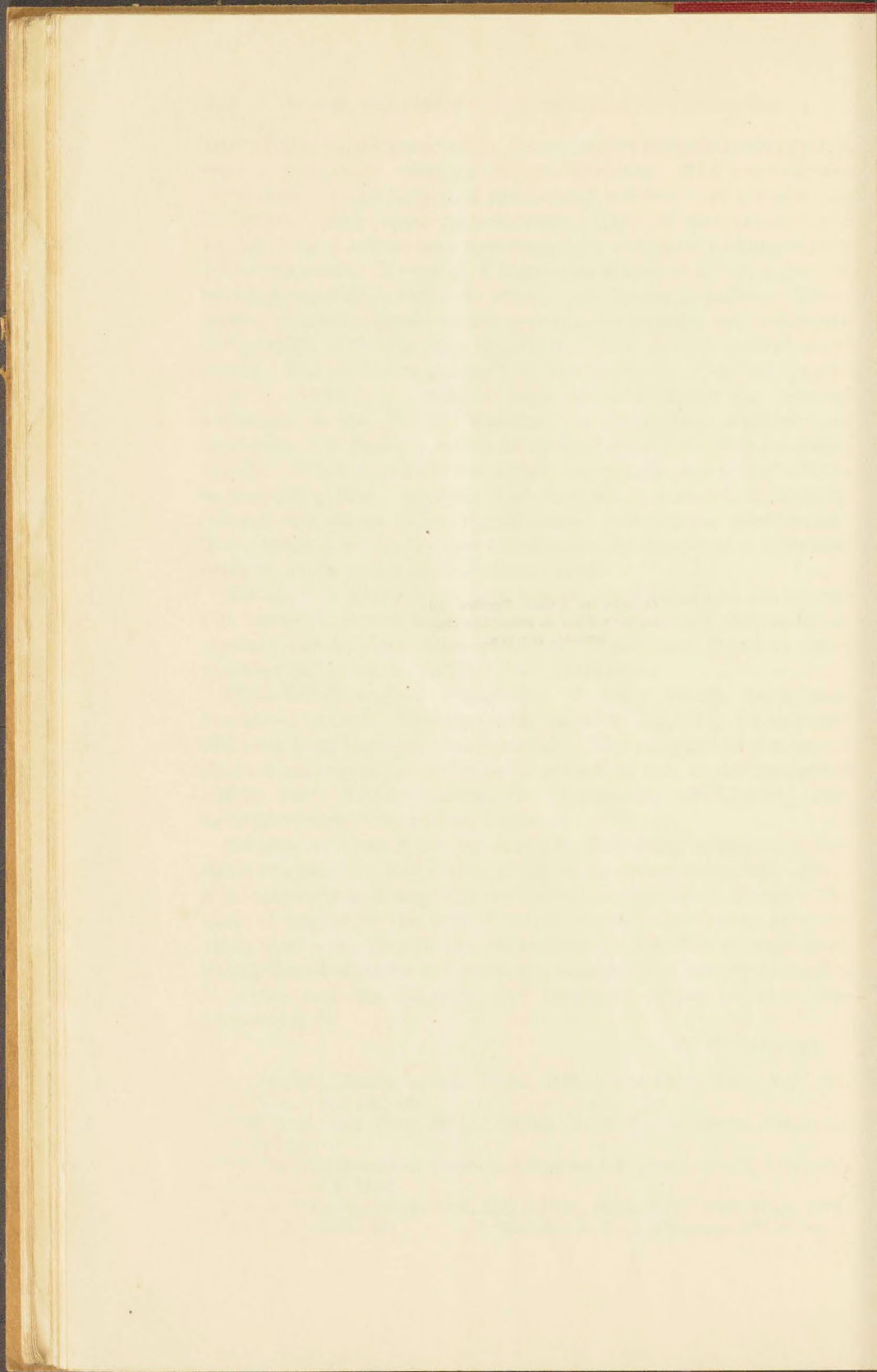
⁹¹ W. T. Schaller, *Amer. Min.*, 1927, 12, 24; H. S. Gale, *Engin. Mining J.*, 1927, 123, 10.

⁹² F. Zambonini and G. Carobbi, *Atti (Rend.) R. Accad. Lincei*, 1926, [vi], 4, 171; *A.*, 1926, 1119.

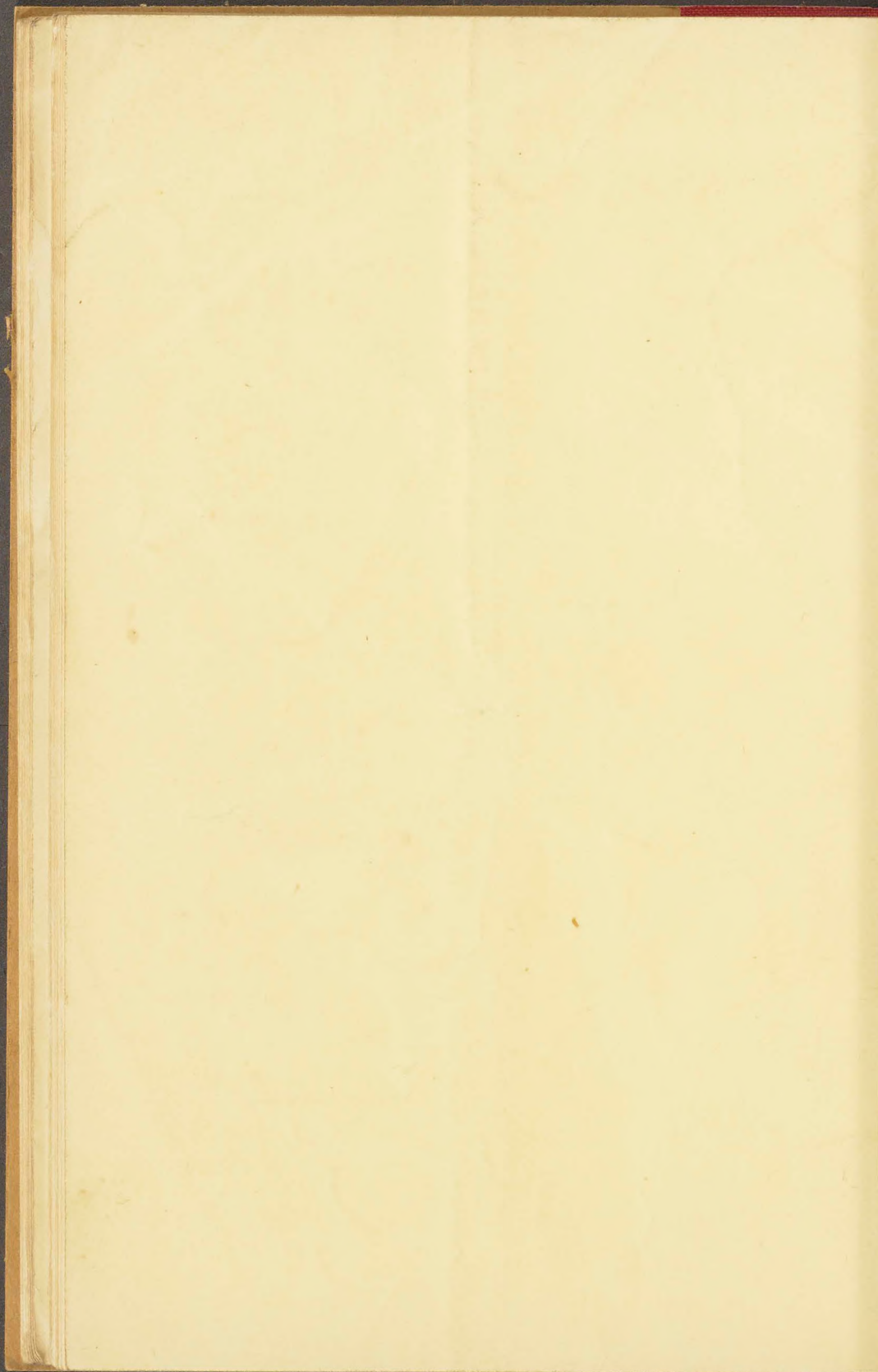
⁹³ L. J. Spencer, *Nature*, 1926, 118, 411; *A.*, 1926, 1022; *Min. Mag.*, 1926, 21, 149; *A.*, 1927, 225.

⁹⁴ Compare A. K. Boldyrev, p. 309 above.

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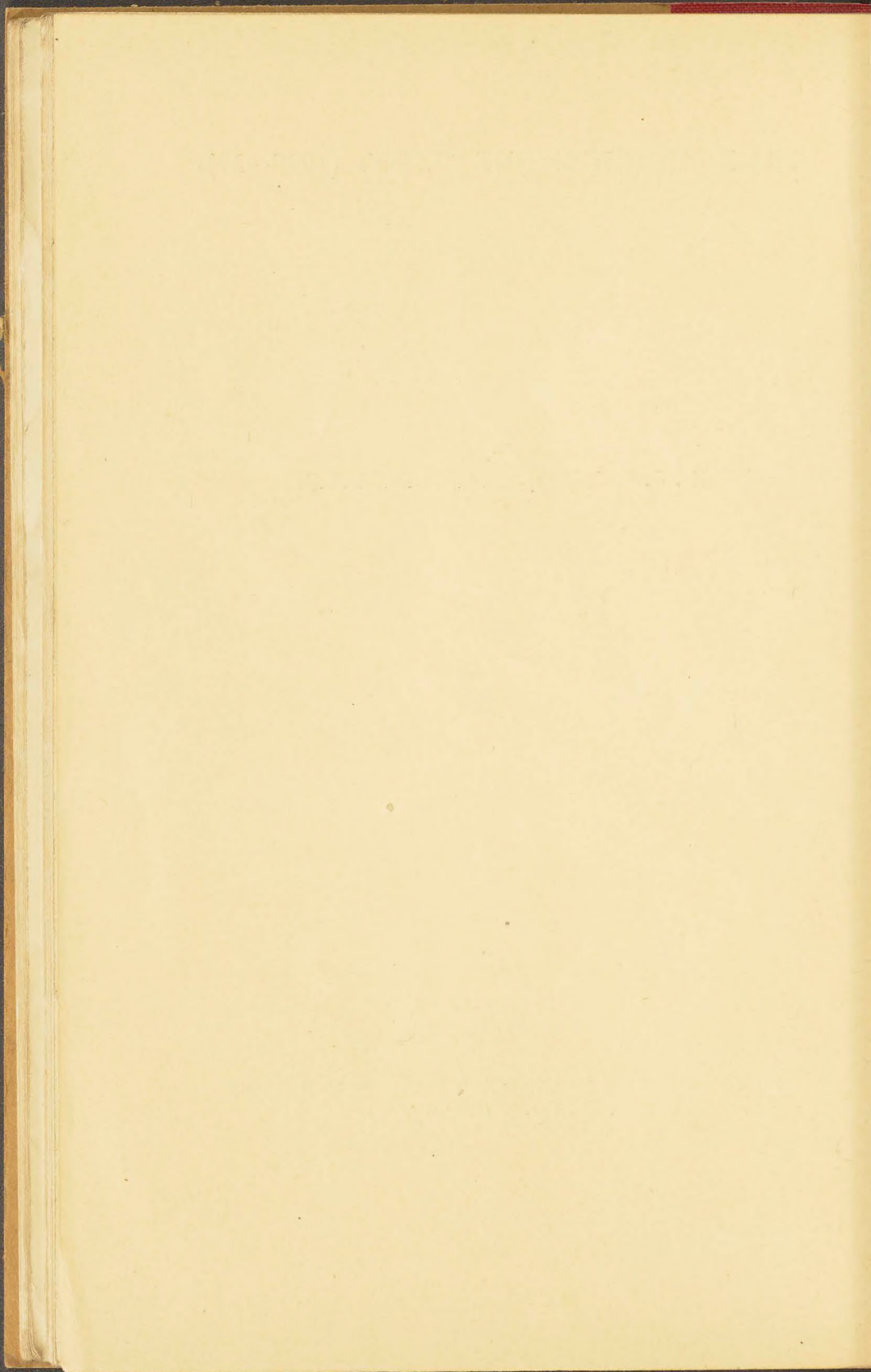
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MINERALOGICAL CHEMISTRY (1928—29).

BY

L. J. SPENCER, M.A., Sc.D., F.R.S.

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MINERALOGICAL CHEMISTRY.

THE new X-ray methods for the investigation of the structure of crystals have given a great and welcome impetus to the more intensive study of minerals. The numerous workers, who are now attacking the many problems by these methods, may be divided into two schools. Physicists, naturally looking at the matter from a physical point of view, are apt to regard each mineral species as a distinct individual—they speak of “this crystal”; and they are usually content to copy from the text-books data for the molecular weight and density on which to base their calculations, regardless of the fact that these may have been determined by mineralogists on different types of material from separate localities, and different again from the material that is being examined afresh by the X-ray methods. The mineralogist, on the other hand, is apt to treat the empirical formulæ of the text-books with less respect, and, being less familiar with the X-ray data, he has more faith in the results of the physicist. He thus attempts to manipulate the chemical formula to fit the X-ray data, whereas the physicist adjusts the X-ray data to fit the formula. A notable exception to such procedure is mentioned below for tremolite in the amphibole group. To correct the long-accepted and apparently simple formula for a common rock-forming mineral is a great triumph for the new X-ray methods.

Minerals have grown under such varied conditions that we cannot assume two crystals of the same species to be exactly alike, unless perhaps they grew side by side in the same rock cavity. Each crystal has, in fact, its own individuality. It is therefore imperative that the material should be examined not by a single method, but also by other methods, and further, on the same sample of material. For this reason many of the isolated determinations—chemical, physical, or X-ray—now published are practically useless for the purpose of any future correlation of data.

Constitution of Silicates.

The atomic structures of a considerable number of silicate minerals have been worked out in detail by X-ray methods by W. L. Bragg and his co-workers at Manchester. These include beryl, phenakite, olivine, monticellite, the humite group, zircon, topaz, staurolite, kyanite, fibrolite, andalusite, diopside, and tremolite. General collected accounts of this important mass of work have been given

by him.¹ Models have been constructed to represent all these structures, and a series of stereoscopic photographs of these and other models has been issued in conjunction with Sir William Bragg.² Two-dimensional pictures of such structures viewed in the usual way often seem to be a mere confused assemblage of balls and rods, but when viewed in the simple folding stereoscope supplied with the photographs they stand out in the solid with remarkable clearness.

A large number of silicates have also been examined by X-ray methods by B. Gossner and his co-workers in Munich. Here, in many cases, the chemical composition and the density have also been determined on the same sample of material. The object of this work has been, not so much to determine the minute structure, but to deduce a chemical formula corresponding with such a molecular weight that a whole number of complete molecules shall be accommodated in the unit cell. The minerals already examined include zunyite, leifite, phenakite and diopase, nepheline, benitoite, scapolite and melilite groups, apophyllite, cordierite, kornerupine, sapphirine, neptunite, epididymite and eudidymite, thortveitite, rhodonite, babingtonite, and several members of the amphibole group. A brief general account of a portion of this work has been given by Gossner.³

With the object of testing the exactness of the stoicheiometric ratios in some common silicate minerals, B. Gossner⁴ and his pupils have made careful analyses in duplicate on specially selected material. In four specimens of olivine from different localities the ratio $\text{SiO}_2 : \text{RO}$ varied from 1 : 1.93 to 1 : 1.99, showing a slight excess of silica over that required by the orthosilicate formula; but when the small amount of water (expelled only at 1100°) is included with the bases the silica shows a slight deficiency, $\text{SiO}_2 : \text{RO}$ then varying from 1 : 2.00 to 1 : 2.05. Three analyses of almandine gave the ratios $\text{R}_2\text{O}_3 : \text{RO} : \text{SiO}_2 = 1 : 2.61 : 2.66$, $1 : 2.61 : 2.71$, and $1 : 2.54 : 2.69$, showing in all cases an excess of both alumina and silica over that required by the garnet formula $\text{R}_2\text{O}_3, 3\text{RO}, 3\text{SiO}_2$ or $3\text{SiO}_3\text{Fe}, \text{Al}_2\text{O}_3$. The excess of alumina is explained by the isomorphous replacement of Al_2 for SiFe (or Al_2O_3 for FeSiO_3) to the extent of 3 mols. %; and the excess of silica over that required for the RSiO_3 portion of the formula may perhaps be explained by its filling in odd spaces in the crystal structure, or perhaps by an isomorphous replacement of silica and aluminium, which differ only

¹ *Proc. Roy. Soc.*, 1927, [A], 114, 450; *A.*, 1927, 501; *Proc. Roy. Inst.*, 1927, 25, 302; *A.*, 1927, 1015; *Trans. Faraday Soc.*, 1929, 25, 291; *A.*, 749.

² First series, 1928; second series, 1929 (Adam Hilger, Ltd., London).

³ *Ber.*, 1928, 61, [B], 1634; *A.*, 1928, 1172.

⁴ *Z. angew. Chem.*, 1929, 42, 175.

slightly in their atomic radii. An analysis of water-clear sanidine showed, on the other hand, a deficiency in silica, namely 1.077 mols. instead of 1.128 required by the feldspar formula.

In certain silicate minerals the small amount of water (1 or 2%), which is expelled only at high temperatures (about 1000°), presents a difficulty in arriving at a satisfactory formula. Such water has often been ignored, being regarded as adsorbed, or present as an adventitious impurity, or due to the incipient decomposition of the mineral. Cases are noted below under amphibole and beryl; and other examples are given by topaz, cordierite, kornerupine, staurolite, etc. It is noted that the X-ray analysis of tremolite now definitely requires the addition of this water in the structure, while apparently in beryl (W. L. Bragg, 1926) the structure can be explained without it. Olivine, always regarded as an anhydrous orthosilicate, also appears to contain some water. B. Gossner⁵ has made special tests for water in perfectly fresh olivines from six localities and found 0.78—1.07%; later tests⁴ on four more olivines showed 0.79—0.83% of water, which is expelled only at 1100°. M. Aurousseau and H. E. Merwin⁶ find only 0.18% of water in olivine from Hawaii.

A recently published book by W. Eitel, "Physikalische Chemie der Silikate" (Leipzig, 1929), deals more especially with the glassy and crystalline conditions of silicates, systems of equilibrium, and the bearing of these on technical problems.

Amphibole Group.—W. Kunitz⁷ gives a long series of sixty-one chemical analyses, together with density and optical determinations for various rock-forming members of the amphibole group. The materials were separated by heavy liquids in a centrifugal apparatus from the finely powdered rocks. Seven isomorphous series are distinguished, and these fall into two groups, namely, those (1—4) from crystalline schists and those (5—7) from igneous rocks.

- (1) Anthophyllite, $H_2Mg_3Si_8O_{24}$ —Grünerite, $H_2Fe_7Si_8O_{24}$.
- (2) Tremolite, $H_2Ca_2Mg_5Si_8O_{24}$ —Actinolite, $H_2Ca_2Fe_5Si_8O_{24}$.
- (3) Glaucophane, $H_2Na_2Mg_3Al_2Si_8O_{24}$ —Riebeckite, $H_2Na_2Fe^{II}_3Fe^{III}_2Si_8O_{24}$.
- (4) Glaucophane, $H_2Na_2Mg_3Al_2Si_8O_{24}$ —Tremolite, $H_2Ca_2Mg_3Mg_2Si_8O_{24}$.
- (5) Common green hornblendes (mixtures of syntagmatite and tremolite-actinolite molecules) $\left\{ \begin{array}{l} H_2Ca_2Mg_4Al_2Si_6O_{22}—H_2Ca_2Fe_4Al_2Si_6O_{22}. \\ H_2Ca_2Mg_5Si_8O_{24}—H_2Ca_2Fe_5Si_8O_{24}. \end{array} \right.$
- (6) Syntagmatitic hornblendes (including pargasite and basaltic hornblende) $\left\{ \begin{array}{l} H_2Ca_2Mg_4Al_2Si_6O_{22}—H_2Ca_2Fe_4Al_2Si_6O_{22}. \\ H_2Ca_2Mg_5Si_8O_{24}—H_2Ca_2Fe_5Si_8O_{24}. \end{array} \right.$
- (7) Alkali-iron-amphiboles (imerinite, hastingsite, katophorite, arfvedsonite) $\left\{ \begin{array}{l} H_2Na_2Mg_4Si_8O_{22}—H_2Na_2Fe_4Si_8O_{22}. \\ H_2Na_2Mg_5Si_8O_{24}—H_2Na_2Fe_5Si_8O_{24}. \end{array} \right.$

⁵ *Centr. Min.*, 1926, [A], 307.

⁶ *Amer. Min.*, 1928, 13, 559.

⁷ *Jahrb. Min., Beil.-Bd.*, 1929, [A], 60, 171;

In several of these series the density and refractive indices show a regular increase with increasing iron content. In the basaltic hornblendes the refractive indices also increase with the percentage of titanium dioxide. The formulæ written in the following manner :

Anthophyllite.....	$[(\text{SiO}_3)_8]\text{H}_2\text{Mg}_2\text{Mg}_2\text{Mg}_3$
Tremolite.....	$[(\text{SiO}_3)_8]\text{H}_2\text{Ca}_2\text{Mg}_2\text{Mg}_3$
Glaucophane.....	$[(\text{SiO}_3)_8]\text{H}_2\text{Na}_2\text{Al}_2\text{Mg}_3$
Syntagmatite.....	$[(\text{SiO}_3)_6(\text{AlO}_2)_2]\text{H}_2\text{Ca}_2\text{Mg}_2\text{Mg}_2$
Arfvedsonite.....	$[(\text{SiO}_3)_6(\text{SiO}_2)_2]\text{H}_2\text{Na}_2\text{Mg}_2\text{Mg}_2$

show more clearly the replacements of $[\text{NaAl}]$ for $[\text{CaMg}]$, of $[\text{NaSi}]$ for $[\text{CaAl}]$, etc. These isomorphous replacements are discussed in connexion with the sizes of atoms, and whether hornblende, augite, or mica should separate from the magma under various conditions.

B. Gossner ⁸ with F. Mussgnug and F. Spielberger have examined various members of the amphibole group, chemically and by X-ray methods, with the idea of adjusting the formulæ so that a whole number of complete molecules shall be contained in the unit cell. By the rotating-crystal method they obtain the following dimensions for the unit cell :

	<i>a.</i>	<i>b.</i>	<i>c.</i>	Axial angle β .
Actinolite	9.91 Å	18.5 Å	5.36 Å.	74° 24'
Glaucophane	9.72	17.89	5.37	74 50
Basaltic hornblende	9.88	18.10	5.31	74 15
Arfvedsonite	9.87	18.31	5.33	"
Barkevikite	9.92	18.30	5.33	"
Kaersutite	9.85	18.17	5.39	"
Aenigmatite	10.02	14.73	5.12	101 58, α and γ about 90°.

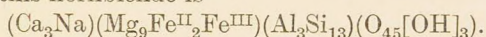
All these, with the exception of aenigmatite, show a close agreement, and they can be referred to the general formula ("Bauplan," or building scheme) $\text{Si}_2\text{O}_6\text{Mg}_2, \text{Si}_2\text{O}_6\text{MgCa}$ [*i.e.*, the tremolite formula $\text{CaMg}_3(\text{SiO}_3)_4$], with four molecules in the unit cell, or eight molecules of the type $\text{R}_2\text{Si}_2\text{O}_6$. Individual analyses are explained by the isomorphous mixing of a great variety of molecules derived by replacement from these two part molecules. For example, $\text{Si}_2\text{O}_6\text{MgCa}$ may be replaced by $\text{Si}_2\text{O}_6\text{Mg}_2$, $\text{Si}_2\text{O}_6\text{Na}_2\text{H}_2$, $\text{Si}_2\text{O}_6\text{Na}_4$, $\text{Si}_2\text{O}_6\text{AlNa}$, and finally by $\text{Al}_2\text{O}_6\text{Na}_2\text{H}_2$; whilst $\text{Si}_2\text{O}_6\text{Mg}_2$ changes with TiO_6Fe_2 , Al_4O_6 , or Fe_4O_6 . In an actual case, the arfvedsonite analysed is represented by the following molecules :

0.190 $\text{Si}_2\text{O}_6\text{Fe}_2$	0.066 $\text{Si}_2\text{O}_6\text{FeCa}$
0.003 Fe_4O_6	0.050 $\text{Si}_2\text{O}_6\text{Fe}(\text{NaH})$
0.007 Al_4O_6	0.011 $\text{Si}_2\text{O}_6\text{Mn}(\text{NaH})$
	0.053 $\text{Si}_2\text{O}_6(\text{NaH})_2$
0.200	0.020 $\text{Si}_2\text{O}_6\text{Na}_4$
	0.200

⁸ *Jahrb. Min., Beil.-Bd.*, 1928, [A], 58, 213; *Centr. Min.*, 1929, [A], 5; *Z. Krist.*, 1929, 72, 111; *A.*, 1223.

Aenigmatite and cossyrite present a difficulty, and various orientations of the crystals and alternative formulæ are tested. With the cell dimensions quoted above, the general formula that appears the most probable is $6\text{SiO}_3\text{Fe}, \text{TiO}_3\text{Fe}$, allowing for two molecules in the unit cell, or seven molecules of the general type $\text{R}_2\text{Si}_2\text{O}_6$. Aenigmatite therefore does not strictly fall into the amphibole group. Similarly, rhodonite,⁹ babingtonite,¹⁰ and wolastonite do not conform with the monoclinic pyroxenes, which contain four molecules of $\text{R}_2\text{Si}_2\text{O}_6$ in the unit cell, nor with the orthorhombic pyroxenes with eight molecules of $\text{R}_2\text{Si}_2\text{O}_6$.

F. Machatschki¹¹ deduces a general formula for the monoclinic amphiboles as $\text{XY}_3(\text{Si}, \text{Al})_4(\text{O}, \text{OH}, \text{F})_{12}$, where $\text{X} = \text{Ca}, \text{Na}, \text{K}$, and $\text{Y} = \text{Mg}, \text{Fe}^{\text{II}}, \text{Fe}^{\text{III}}, \text{Al}$, also Ti and Mn . The special case discussed is based on the chemical analysis of a hypersthene-hornblende rock from Greenland, and after deducting 16% of hypersthene and neglecting small amounts of olivine and iron ores, the special formula deduced for this hornblende is



The mutual replacement of atoms in the "X" and "Y" groups and of Al for Si depends, not on their valencies, but on their sizes being such that they will fit into the crystal structure, with a certain accommodation between different pairs, for example, Al for Si together with OH for O. The assumption of the replacement of aluminium for silicon is made to account for the occasional deficiency in silica below the metasilicate ratio; but it seems curious to think of aluminium taking the part of silicon in a silicate. Any variation shown by analyses from the ratio $\text{X} : \text{Y} = 1 : 3$ is further explained by an interchange of atoms between these two groups. Obviously by shuffling atoms about in this way any analysis might be fitted in with any formula.

B. E. Warren¹² has determined for tremolite from New York the cell dimensions $a = 9.78$, $b = 17.8$, $c = 5.26$ Å. ($a : b : c = 0.550 : 1 : 0.295$, $\beta = 73^\circ 58'$), with two molecules $\text{H}_2\text{Ca}_2\text{Mg}_5(\text{SiO}_3)_8$ in the unit cell. Except for the double length of the b -axis, these dimensions are very close to those of diopside,¹³ and with certain modifications, the arrangement of the atoms is very similar in the two minerals. Tetrahedral groups of four oxygen atoms surrounding each silicon atom are linked by shared oxygens to form endless chains parallel to the vertical c -axis of the crystal. In tremolite

⁹ B. Gossner and K. Brückl, *Centr. Min.*, 1928, [A], 316; A., 495.

¹⁰ B. Gossner and F. Mussnug, *ibid.*, 1928, [A], 274; A., 382.

¹¹ *Z. Krist.*, 1929, **71**, 219.

¹² *Ibid.*, **72**, 42; *Abs. Theses Mass. Inst. Tech.*, 1929, No. 4, 74; A., 1130.

¹³ B. E. Warren and W. L. Bragg, *Z. Krist.*, 1928, **69**, 168; A., 1223.

two such diopside chains are linked together and there are four chains in the unit cell. The calcium and magnesium atoms, all lying on diad axes, are surrounded by eight and six oxygens respectively. Such a structure will accommodate only ten magnesium atoms in the unit cell, and the two extra ones required by the usually-accepted formula $\text{CaMg}_3(\text{SiO}_3)_4$ are replaced by four (OH) groups, which occupy the same space as four oxygen atoms. The new formula, requiring 2.2% of H_2O , agrees well with the best published analyses when these are recalculated with small isomorphous replacements (Si,Al), (Mg,Fe), (Ca,Na,K), and (OH,F); but the presence of water was not actually proved in the sample of material used for the X-ray analysis. This crystal structure explains the fibrous texture of the mineral, which is very prominent in the amphibole-asbestos variety, and the prism-cleavage of 56° .

This new formula, $\text{H}_2\text{Ca}_2\text{Mg}_5(\text{SiO}_3)_8$, for tremolite, deduced from a consideration of the crystal structure as determined by X-ray methods, is identical with that arrived at independently and by quite another method by W. Kunitz (see above), and it seems to be fully established. The apparently simple formula $\text{CaMg}_3(\text{SiO}_3)_4$ for this common rock-forming mineral has been familiar in the textbooks since the third edition (1850) of Dana's "System of Mineralogy." P. A. von Bonsdorff in 1821 found about 1% of fluorine and water in tremolite; Penfield and Stanley (1907) found 2.03%; Allen and Clement (1908) 2.31—3.04%; and W. Kunitz (1929) 1.97—2.28% in actinolite. This water is expelled only at temperatures up to 1000° . Penfield and Stanley accounted for it, partly in a bivalent group $\text{R}^{\text{III}}\text{O}(\text{F},\text{OH})_2$, and partly as acid hydrogen in their general formula $\text{H}_8\text{Si}_4\text{O}_{12}$ for the "amphibole acid," which was supposed to have a controlling influence ("mass effect") on the isomorphous replacements. Allen and Clement regarded the water as "dissolved" in the crystal and not chemically combined. The new formula appears to have been first given by P. Niggli in the second edition of his "Lehrbuch der Mineralogie" (1926, vol. 2, p. 468), where, after quoting the usual formula, he remarks that part of the magnesium is almost always replaced by hydrogen and that many analyses agree well with the formula $[\text{SiO}_4, \text{SiO}_2]_4\text{Ca}_2\text{Mg}_5\text{H}_2$. In a rather more obscured form it was earlier given by B. Gossner¹⁴ as $[\text{2SiO}_3\text{Ca}, 4\text{SiO}_3\text{Mg}], [\text{2SiO}_2, \text{MgO}_2\text{H}_2]$, which reduces to $\text{H}_2\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{24}$.*

S. Kôzu¹⁵ has found that when common hornblende is heated to

¹⁴ *Z. Krist.*, 1924, **60**, 364.

¹⁵ S. Kôzu, B. Yoshiki, and K. Kani, *Sci. Rep. Tôhoku Imp. Univ.*, 1927, [3], **3**, 143.

* Note added in proof.—The formula $8\text{SiO}_2, 5\text{MgO}, 2\text{CaO}, \text{H}_2\text{O}$ was suggested by W. T. Schaller, *Bull. U.S. Geol. Survey*, 1916, **610**, 136; *A.*, 1916, ii, 631.

750° there is a marked contraction in volume and a sudden change in the optical constants, the material being then changed into the high-temperature modification corresponding with basaltic hornblende. This change appears to be of some structural significance.

Apophyllite.—New analyses of apophyllite from various localities by B. Gossner and O. Kraus¹⁶ show that small amounts of fluorine are invariably present. A new formula is written in the form $4[\text{H}_2\text{Si}_2\text{O}_5, \text{Ca}(\text{OH})_2], \text{KF}$, in which part of the fluorine is replaced by hydroxyl and a small amount of potassium by sodium. The water commences to be lost only at 245° with a destruction of the crystal structure, and it does not behave like water of crystallisation or zeolitic water. X-Ray examination gives a unit tetragonal cell of dimensions $a = 12.73$, $c = 15.84$ Å., containing four molecules. The pronounced optical anomalies are explained by the partial replacement of fluorine by hydroxyl, the difference in volume of these constituents causing a strain in the crystal structure.

Andalusite, Fibrolite, and Kyanite.—These trimorphous aluminium silicates, though very different in their physical characters, are found by X-ray analysis to have much the same size of unit cell, containing in each case four molecules Al_2SiO_5 . In the following table of the cell dimensions those of topaz are added for comparison.

	<i>a</i> .	<i>b</i> .	<i>c</i> .	Space-group.
Andalusite ¹⁷	7.76 Å.	7.90 Å.	5.56 Å.	V_h^{12}
Fibrolite ¹⁸	7.43	7.58	5.74	V_h^{16}
Kyanite ¹⁹	7.09	7.72	5.56	?
„ ²⁰	7.122	7.883	5.650	?
Topaz ²¹	4.64	8.78	8.38	V_h^{16}

These minerals, which with the exception of kyanite are all orthorhombic, show several curious relations that have not yet been elucidated. Andalusite has a certain crystallographic relation to topaz; and the manganiferous variety “viridine” has on optical grounds been regarded as a distinct species. Fibrolite also has a peculiar satellite “mullite,” the structure of which cannot be distinguished from that of fibrolite. The chemical formula $\text{Al}_6\text{Si}_2\text{O}_{13}$

¹⁶ *Z. Krist.*, 1928, **68**, 595; *A.*, 1036.

¹⁷ W. H. Taylor, *ibid.*, 1929, **71**, 205.

¹⁸ *Idem*, *ibid.*, 1928, **68**, 503.

¹⁹ W. L. Bragg and J. West, *Proc. Roy. Soc.*, 1927, [A], **114**, 450; *A.*, 1927, 501; W. H. Taylor and W. W. Jackson, *ibid.*, 1928, [A], **119**, 132; *A.*, 1928, 693; S. Náráy-Szabó, W. H. Taylor, and W. W. Jackson, *Z. Krist.*, 1929, **71**, 117.

²⁰ C. M. Cardoso, *Fortschr. Min. Krist. Petr.*, 1927, **12**, 18; *Ber. Sächs. Akad. Wiss.*, 1928, **80**, 165; E. Schiebold and C. M. Cardoso, *Fortschr. Min. Krist. Petr.*, 1929, **13**, 61.

²¹ N. A. Alston and J. West, *Proc. Roy. Soc.*, 1928, [A], **121**, 358; *Z. Krist.*, 1928, **68**, 149; *A.*, 15.

assigned to "mullite" is explained as perhaps due to the partial replacement of silicon atoms by aluminium atoms in the fibrolite structure.¹⁸ In the triclinic kyanite the angles between the crystallographic axes and the edges of the unit cell are $\alpha = 90^\circ 51\frac{1}{2}'$, $\beta = 101^\circ 2'$, $\gamma = 105^\circ 44\frac{1}{2}'$; but other axes can be chosen, all approximately at right angles, namely, $\alpha = 90^\circ 51\frac{1}{2}'$, $\beta = 90^\circ 5'$, $\gamma = 90^\circ 27'$, the dimensions of this pseudo-rhombic cell being $a' = 26.868$, $b' = 7.883$, $c' = 5.650$ Å. This corresponds with a slightly distorted close-packed cubic structure marked out by the oxygen atoms. Oxygen atoms are grouped tetrahedrally around the silicon atoms, and octahedrally around the aluminium atoms, as in topaz (p. 265) and staurolite (p. 265).

Beryl.—A set of detailed analyses²² made on beryls of different types shows considerable deviations from the usually accepted formula $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$. The pink tabular crystals of the "rosterite" variety from Elba contain appreciable amounts of alkalis (Li_2O 0.43, Na_2O 4.22, K_2O 2.25, Cs_2O 0.91%) together with water 0.84%. "Emerald" from Colombia gave less alkalis (0.88%), but more water (1.84%), together with Cr_2O_3 0.077%, accounting for the colour; and clear blue "aquamarine" from Siberia gave alkalis 1.04%, water 0.98%. The variations in composition are explained by assuming mixtures with the main molecule $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ of molecules R_2SiO_3 and $\text{R}_2\text{Al}_2\text{Si}_2\text{O}_8$, where R_2 is Li_2 , Na_2 , K_2 , Cs_2 , together with some Be, Ca, Mg. Small amounts of alkalis and water have also been found in beryl from Japan.²³

Certain transparent green beryls when heated to 400–450° change in colour to blue;²⁴ and this is now much used in the trade or improving the colour of these gem stones.

Epididymite and Eudidymite.—These rare dimorphous minerals with the composition $\text{HNaBeSi}_3\text{O}_8$ are found by X-ray methods to have unit cells of very nearly the same dimensions:

	a.	b.	c.	Mol. vol.	Space-group.
Epididymite ²⁵ ...	12.65 Å	7.41 Å	13.53 Å.	158.5	V_h^{17}
Eudidymite ²⁶ ...	12.70	7.34	14.01	159.3	C_{2h}^6

In each case the unit cell contains eight molecules and the arrangement of the atoms is probably much the same. There is, however, a wide difference in the axial angle, epididymite being orthorhombic

²² F. Zambonini and V. Caglioti, *Gazzetta*, 1928, 58, 131; *A.*, 1928, 731.

²³ T. Uemura, *Japan. J. Chem.*, 1926, 2, 117; *A.*, 1928, 1211; J. Yoshimura, *Bull. Chem. Soc. Japan*, 1926, 1, 239; *A.*, 1927, 129.

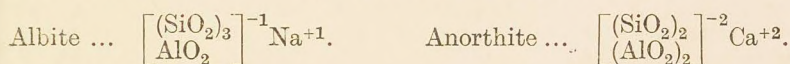
²⁴ J. Kurbatov and W. Kargin, *Centr. Min.*, 1927, [A], 361; *A.*, 1928, 730.

²⁵ B. Gossner and F. Mussnug, *Festschr. V. Goldschmidt*, Heidelberg, 1928, 117.

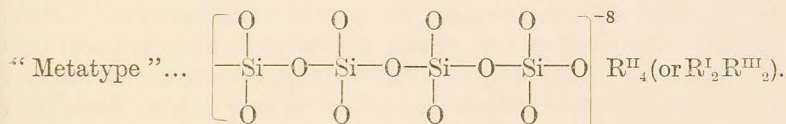
²⁶ B. Gossner and O. Kraus, *Centr. Min.*, 1929, [A], 257.

($\beta = 90^\circ$) and eudidymite monoclinic with $\beta = 77^\circ 26'$. This low degree of polymorphism is somewhat similar to that of α - and β -quartz.

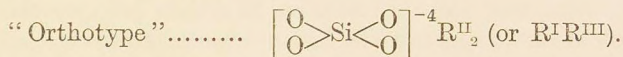
Felspar Group.—F. Machatschki²⁷ points out that W. Wahl's co-ordination formulæ (*Ann. Reports*, 1927, **24**, 294) for albite $[\text{Al}_2(\text{SiO}_3)_2(\text{Si}_2\text{O}_5)_2]\text{Na}_2$ and anorthite $[\text{Al}_2\text{O}_2(\text{SiO}_3)_2]\text{Ca}$ do not explain the isomorphism of this pair of minerals in the series of plagioclase feldspars. As the fundamental unit of silicate structures, he takes a tetrahedral group of four O^{-2} ions around a Si^{+4} ion. Aluminium Al^{+3} with O^{-2} may have a co-ordination number 4 or 6, and when 4 it may take the place of silicon in the tetrahedral group of oxygens. Similarly, Be^{+2} and perhaps B^{+3} may also occupy this position. Since tetrahedra cannot fill space, the cavities between them may be occupied by the metal ions. In the felspar type of silicate structure (where $\text{Si} + \text{Al} : \text{O} = 1 : 2$) every oxygen ion is common to two adjacent tetrahedra, and the "formulæ" are written



Formulæ on similar lines are also suggested by Machatschki for the metasilicates and the orthosilicates. In his "metatype," with SiO_3 or AlO_3 , two oxygen ions are in common for adjacent tetrahedra, and an endless chain (similar to that deduced by B. E. Warren and W. L. Bragg for the pyroxenes and amphiboles, p. 257) is represented by



In his "orthotype" there is no linking of oxygen ions in adjacent tetrahedra, and here separate molecules can exist, the formula being then of the ordinary co-ordination kind.



In the "felspar type" and the "metatype" the structures are continuous and there are no separate molecules. These are the "open structures" of W. L. Bragg and J. West,²⁸ which include quartz, beryl, phenakite, etc. For beryl, the metatype formula is written as $[(\text{SiO}_2)_6(\text{BeO}_2)_3]^{-6} \text{Al}^{+3}\text{Al}^{+3}$.

The unit cell dimensions of the various feldspars, as determined by

²⁷ *Centr. Min.*, 1928, [A], 97; *A.*, 1928, 1349.

²⁸ *Proc. Roy. Soc.*, 1927, [A], **114**, 469; *A.*, 1927, 501.

E. Schiebold,²⁹ are tabulated below. The base-centred cell contains four molecules KAlSi_3O_8 (orthoclase), $\text{NaAlSi}_3\text{O}_8$ (albite), or $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite). In the plagioclase feldspars, the substitution of Na-Si for Ca-Al in passing from albite to anorthite is accompanied by a small contraction of the lattice, the greatest variation being in the *c*-axis. The change of the molecular volume is, however, not an exact linear function of the chemical composition, there being a maximum at the albite-anorthite mixture 1 : 1, corresponding with labradorite. The entry of potassium causes a considerable enlargement of the lattice dimensions, the *a*-axis showing the greatest change whilst the *c*-axis is here little affected. The X-ray examination emphasises the pseudo-cubic character of the feldspars, and the structure can be considered as based on a close-packed arrangement of 32 oxygen atoms.

	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>a.</i>	<i>β.</i>	<i>γ.</i>
Adularia	8.61Å.	13.07Å.	7.26Å.	90° 0'	116° 3'	90° 0'
Sanidine	8.42	12.92	7.14	90 0	115 35	90 0
Microcline	8.44	13.00	7.21	90 7	115 50	89 55
Hyalophane...	8.50	12.92	7.12	90 0	115 35	90 0
Albite	8.23	13.00	7.25	94 3	116 29	88 9
Oligoclase ...	8.16	12.90	7.13	93 4	116 22	90 4
Labradorite...	8.23	12.91	7.16	93 31	116 3	89 57
Anorthite ...	8.185	12.895	7.09	93 13	116 55	91 12

The feldspars have been studied from many points of view. They are important constituents of most kinds of igneous rocks, and the classification of such rocks is in part based on the kind of feldspar that they contain. Ready means for the determination of the feldspars are therefore needed. Graphs plotting the variation of the various optical data with the chemical composition are given in the text-books on petrography and rock-forming minerals. The several graphs of refractive indices and chemical composition have been examined critically by H. L. Alling,³⁰ and collecting together the data on which these have been based, he finds that in many cases they depend on old and untrustworthy chemical analyses, and that the optical data have not always been determined on the material actually analysed. Much attention has been paid to the determination of the feldspars by the Fedorov method with the aid of the universal microscope stage. The feldspar in a thin rock-slice is covered with a glass hemisphere of nearly the same refractive index as that of the mean of the mineral, and it can be brought into any desired position by rotation about three axes at right angles, these axes being provided with graduated circles. By this means the

²⁹ *Fortschr. Min. Krist. Petr.*, 1927, **12**, 78; 1929, **14**, 62; *Trans. Faraday Soc.*, 1929, **25**, 315; *A.*, 749.

³⁰ *J. Geol.*, 1929, **37**, 462.

different types of twinning, the orientation of the three principal directions of vibration, and the optic axial angle can be determined and plotted on graphs. This method has been largely developed by L. Duparc and his pupils in Geneva, and a summary of recent work is given in "Mineralogical Abstracts,"³¹

The feldspar diagram orthoclase-albite-anorthite has been studied in detail by J. H. L. Vogt.³² Various equilibrium diagrams are given, and he tabulates the Or : Ab : An ratios in the rock, in the separated feldspars, and in the residual magma. Finally, the feldspars have been studied from the point of view of their application in ceramics, enamel-ware, etc.³³

Melilite Group.—The following X-ray data have been determined by B. Gossner and F. Mussnug :³⁴

	Mols. in unit cell.	<i>a</i> .	<i>c</i> .
Gehlenite ...	4 Mols. $\text{SiO}_4\text{Ca}_2\text{Al}_2\text{O}_3$	11.11 Å	5.06 Å.
Melilite	4 Mols. $\text{CaO}, \text{Si}_2\text{O}_6\text{CaMg}$	11.12	5.09
Sarcosite	6 Mols. $\text{Si}_2\text{O}_6\text{AlNa}, \text{Si}_2\text{O}_6\text{Al}_2\text{Ca}, 3\text{CaO}$	17.6	15.59

Gehlenite and melilite, both with the space-group D_{4h}^3 , are thus closely related, and their composition is expressed as mixtures of the molecules $\text{CaO}, \text{SiO}_3\text{Ca}, \text{Al}_2\text{O}_3$ (velardeñite), $\text{CaO}, \text{SiO}_3\text{Ca}, \text{SiO}_3\text{Mg}$ (åkermanite), and $\text{CaO}, \text{SiO}_3\text{NaSiO}_3\text{Al}$, in which there may also be replacements $\text{Al}_2 = \text{SiMg}$, $\text{CaMg} = \text{NaAl}$, and $\text{SiNa} = \text{AlCa}$. On the other hand, sarcosite, with space-group C_{4h}^3 , is more closely related to the scapolite group, and the composition is expressed as an addition compound of scapolite ($3\text{Si}_2\text{O}_6\text{Al}_2\text{Ca}, \text{CaO}$) with $3\frac{1}{2}\text{CaO}$.

From a consideration of the published analyses of the minerals åkermanite, humboldtilite, melilite, gehlenite, and sarcosite, H. Berman³⁵ deduces a general formula for the whole group as $(\text{Ca} + \text{Na})_{20-x}\text{Mg}_y\text{Al}_z\text{Si}_{30-(y+z)}\text{O}_{70}$, where $x = 0$ to 3, $y = 0$ to 10, and $z = 0$ to 20. End members of the series are: åkermanite, $\text{Ca}_2\text{MgSi}_2\text{O}_7$; gehlenite, $\text{Ca}_2\text{Al}_2\text{SiO}_7$; soda-melilite, $\text{Na}_2\text{Si}_3\text{O}_7$; and sub-melilite, CaSi_3O_7 .

Mica Group.—J. Jakob³⁶ has continued his work of laboriously analysing a large number of micas, giving also in some cases optical data for the material analysed, but no density determinations. Since the last Report he has made 28 new analyses of muscovites and

³¹ *Min. Mag.*, 1928, Abstr., 3, 515.

³² *Skrifter Norske Vidensk. Akad.*, 1926, No. 4.

³³ *B.*, 1928, 53, 193, 263.

³⁴ *Centr. Min.*, 1928, [A], 129, 167.

³⁵ *Amer. Min.*, 1929, 14, 389.

³⁶ *Z. Krist.*, 1928, 69, 217; 1929, 69, 403, 511; 1929, 70, 493; 1929, 72, 327; *A.*, 1263.

phlogopites. For individual specimens such formulæ as the following are deduced for muscovite and phlogopite respectively :

$$\begin{aligned}
 29.98 \left[\text{Al}(\text{SiO}_6\text{SiO}_2)_3 \right] \begin{matrix} \text{Al}_5 \\ \text{K}_{3.198} \\ \text{H}_{2.802} \end{matrix} + 25.19 \left[\text{Al}(\text{SiO}_4\text{SiO}_2)_3 \right] \begin{matrix} \text{Al}_2 \\ \text{K}_{1.599} \\ \text{H}_{1.401} \end{matrix} + 44.83 \left[\text{Al}(\text{SiO}_5\text{SiO}_2)_3 \right] \begin{matrix} \text{Al}_2 \\ \text{K}_{1.599} \\ \text{H}_{4.101} \\ \text{Mg}_{1.650} \end{matrix} \\
 59.97 \left[\text{Al}(\text{SiO}_4)_3 \right] \begin{matrix} \text{Al}_2 \\ \text{K}_{1.993} \\ \text{H}_{1.007} \end{matrix} + 20.17 \left[\text{Mg}(\text{SiO}_5)_3 \right] \begin{matrix} \text{Mg}_{7.566} \\ \text{H}_{0.888} \end{matrix} + 19.86 \left[\text{Mg}(\text{SiO}_6)_3 \right] \begin{matrix} \text{Mg}_{7.566} \\ \text{H}_{2.868} \end{matrix}
 \end{aligned}$$

W. Kunitz³⁷, seeing that some of his analyses do not check with those of Jakob made on material from the same locality, has repeated his work and finds that calcium enters only occasionally in very small amounts into the composition of muscovite and biotite.

The composition of the micas has been further discussed by A. N. Winchell³⁸ and A. F. Hallimond,³⁹ the debatable points being whether the ratio $\text{K}_2\text{O} : \text{SiO}_2$ is constant or not at 1 : 6, and whether Al_2O_3 replaces RO or MgSiO_3 .

X-Ray examinations of the micas have so far led to no definite results. The superposed lamellæ show rotations and oblique translations and the data obtained do not appear to give the true crystal lattice.⁴⁰

Nepheline.—J. Morozewicz⁴¹ reviews recent work on the composition of nepheline and adheres to the formula he proposed in 1907, namely $\text{K}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot n\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$, where n is usually 4 but may vary to 6. This is regarded as a double salt rather than an isomorphous replacement of potassium and sodium. Four new analyses of elæolite are in agreement with this formula. The rocks from which the analysed mineral was separated show a range of silica from 54.95 to 62.86%, and the $\text{K}_2\text{O} : \text{Na}_2\text{O}$ ratio ranges from 1 : 2.3 to 1 : 23.6. In spite of this variation in composition of the magma from which the mineral crystallised, the $\text{K}_2\text{O} : \text{Na}_2\text{O}$ ratio in the mineral varies only from 1 : 4 to 1 : 4.5.

X-Ray examination of water-clear nepheline from Vesuvius by B. Gossner⁴² gave a unit hexagonal cell of dimensions $a = 10.05$, $c = 8.43 \text{ \AA}$., and containing twelve molecules $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$. Etch-figures suggest that nepheline belongs to the hexagonal-pyramidal class, whilst the other physical characters suggest the dihexagonal-bipyramidal class. The X-ray data point to the latter with the

³⁷ *Z. Krist.*, 1929, **70**, 508.

³⁸ *Amer. Min.*, 1927, **12**, 267; 1928, **13**, 52, 567.

³⁹ *Ibid.*, 1927, **12**, 413; 1928, **13**, 451.

⁴⁰ C. Mauguin, *Compt. rend.*, 1928, **186**, 879; *A.*, 1928, 463; C. Mauguin and L. Graber, *ibid.*, 1928, **186**, 1131; *A.*, 1928, 611; C. Mauguin, *ibid.*, 1928, **187**, 303; *A.*, 1928, 1077; C. Mauguin, *Bull. Soc. franç. Min.*, 1928, **51**, 285.

⁴¹ *Bull. Acad. Polonaise*, 1928, [A], 111; *A.*, 45.

⁴² *Centr. Min.*, 1927, [A], 150.

space-group C_{6h}^2 . C. Gottfried⁴³ finds a unit hexagonal cell $a = 10.09$, $c = 8.49$ Å. containing twenty-four molecules NaAlSiO_4 , and space-group C_6^2 .

Staurolite.—The following X-ray determinations by different authors show a close agreement in the dimensions of the unit cell, but there are considerable differences in the chemical formula. No new analyses or density determinations have been made of the material examined.

	Mols. in unit cell.	<i>a</i> .	<i>b</i> .	<i>c</i> .	Space-groups.
(1) ⁴⁴	2 Mols. $\text{HFe}_2\text{Al}_9\text{Si}_4\text{O}_{24}$	7.84 Å	16.52 Å	5.61 Å.	V_h^{11}
(2) ⁴⁵	4 Mols. $\text{HFeAl}_3\text{Si}_2\text{O}_{13}$	7.81	16.59	5.64	V_h^{17}
(3) ⁴⁶	4 Mols. $\text{H}_2\text{FeAl}_4\text{Si}_2\text{O}_{12}$	7.82	16.52	5.63	V_h^{17}

Selecting fresh axes and another unit cell for kyanite, Cardoso⁴⁵ traces a relation between kyanite and staurolite for the purpose of explaining the regular intergrowth of these two minerals. Náray-Szabó⁴⁶ also suggests a relation between the structures of kyanite and staurolite, and supposes the staurolite structure to be represented by alternate slabs of $\text{Fe}(\text{OH})_2$ and $2\text{Al}_2\text{SiO}_5$ (kyanite).

Topaz.—A unit cell of dimensions $a = 4.64$, $b = 8.78$, $c = 8.37$ Å. and containing four molecules $[\text{Al}(\text{F},\text{OH})_2]\text{SiO}_4$ was deduced by J. Leonhardt in 1923 for topaz from San Luis Potosi, Mexico. L. Pauling,⁴⁷ using the co-ordination theory of ionic crystals, assumed the fundamental polyhedra for topaz to be an octahedron of oxygen and fluorine anions surrounding each aluminium ion, and a tetrahedron of oxygen ions about each silicon ion. The structure so deduced agrees with the data of Leonhardt. This has been confirmed by N. A. Alston and J. West,⁴⁸ who find for topaz from Nigeria the unit cell dimensions $a = 4.64$, $b = 8.78$, $c = 8.38$ Å. The close agreement in these figures for material from different localities is remarkable when we consider that topaz may range in chemical composition from fluor-topaz $(\text{AlF})_2\text{SiO}_4$ to hydroxy-topaz $(\text{AlOH})_2\text{SiO}_4$ and in density from 3.35 to 3.65. Colourless to faint bluish or greenish crystals are abundant in the alluvial tin deposits of Northern Nigeria; but this material has never been analysed chemically. From determinations of the refractive indices ($\alpha = 1.615$ — 1.621 , $\beta = 1.622$ — 1.628) and optic axial angle ($2V = 64^\circ 28'$ — $65^\circ 54'$), A. Schoep⁴⁹ concludes that these crystals are fluor-topaz containing about 20% of fluorine.

⁴³ *Z. Krist.*, 1927, **65**, 100.

⁴⁴ C. Gottfried, *ibid.*, **66**, 103.

⁴⁵ Refs. as (20).

⁴⁶ S. Náray-Szabó, *Z. Krist.*, 1929, **71**, 103.

⁴⁷ *Proc. Nat. Acad. Sci.*, 1928, **14**, 603; *A.*, 1928, 1176.

⁴⁸ *Proc. Roy. Soc.*, 1928, [A], **121**, 358; *A.*, 15; *Z. Krist.*, 1928, **69**, 149

⁴⁹ *Natuurwetensch. Tijds.*, 1928, **10**, 3; *A.*, 1928, 503.

Tourmaline.—W. Kunitz⁵⁰ gives twenty new chemical analyses, together with density and refractive index determinations, for tourmalines from various localities. He divides them into two series: the dravite series of magnesium-iron tourmalines, and the rubellite series of lithium-iron tourmalines; and the chemical composition is explained by the isomorphous mixing of the following molecules:

(1) Dravite molecule	$H_8Na_2Mg_6Al_{12}Si_{12}B_6O_{62}$
(2) Schorl "	$H_8Na_2Fe_6Al_{12}Si_{12}B_6O_{62}$
(3) Rubellite "	$H_8Na_2[LiAl]_3Al_{12}Si_{12}B_6O_{62}$
(4) "Uvite" "	$H_8Ca_2Mg_6Al_{10}Si_{12}B_6O_{62}$
(5) "Tsilaïs site" molecule.....	$H_8Na_2Mn_6Al_{12}Si_{12}B_6O_{62}$
(6) (Higher alumina).....	$H_8Na_2Fe_8Al_{14}Si_{11}B_6O_{62}$

In most cases the composition can be explained by a mixture of two of these molecules: (1) and (2) for the dravite series, and (2) and (3) for the rubellite series. In both these series the density and refractive indices show a regular increase with the increase of the schorl or iron molecule. In the dravite series the vertical crystallographic axis *c* shows a slight decrease with increasing iron content. The extra molecules (4), (5), and (6) are invoked to explain the composition of tourmalines richer in calcium (up to 5.35% CaO), manganese (up to 8.21% MnO), and aluminium. The lithium in the rubellite molecule is quite distinct from the other alkali metals, and it forms a group [LiAl] replacing [MgMg], similar to the replacement of [LiAl] for [CaMg] in the pyroxenes and of [Li₂Si] for [Fe^{II}]₃ in the lithia micas. These replaceable groups have the same sum of the valencies and nearly the same sum of atomic volumes. The above formulæ are intended to express the close relationship between the tourmalines and the micas.⁵¹ These minerals occur in intimate association in rocks, and tourmaline is often found altered to mica.

F. Machatschki⁵² from a collection of published analyses deduces, on the same lines as he did for the monoclinic amphiboles and pyroxenes (p. 257), a general formula for tourmaline as $XY_9B_3Si_6H_xO_{31}$, where X = Ca, Na, and some Mn^{II}, and Y = Li, Mg, Mn, Fe, Al. Special formulæ to fit particular analyses range from $Ca_3(Mg_{10}Al_{17})B_9Si_{18}H_{10}O_{93}$ to $Na_3(LiAl_{26})B_9Si_{18}H_5O_{93}$. From X-ray rotation photographs he gets for different tourmalines dimensions ranging from $a = 15.81$, $c = 7.10$ Å. to $a = 16.02$, $c = 7.22$ Å. for the unit hexagonal cell containing three molecules $XY_9B_3Si_6H_xO_{31}$, but the number of atoms is too complex for any attempt at their grouping.

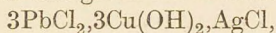
⁵⁰ *Chem. Erde*, 1929, **4**, 208; *A.*, 905.

⁵¹ W. Kunitz, *Fortschr. Min. Krist. Petr.*, 1927, **11**, 313; *A.*, 1928, 148.

⁵² *Z. Krist.*, 1929, **70**, 211.

Miscellaneous Minerals.

Boleite and Cumengeite.—Preliminary results⁵³ of an X-ray examination of boleite gave a cubic unit cell of edge 15.6 Å. containing thirty-two molecules $\text{PbCl}_2 \cdot \text{Cu}(\text{OH})_2$. A new analysis of cubo-octahedral crystals has given the formula



and further X-ray examination shows a unit cube of edge 15.40 Å. containing nine such molecules.⁵⁴ Cumengeite⁵⁴ occurs as tetragonal pyramids on the six faces of cubes of boleite. Analysis gave the formula $4\text{PbCl}_2 \cdot 4\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$, and the cell dimensions are $a = 15.17$, $c = 24.71$ Å. Calculation gives eleven such molecules in the unit cell, but this number does not agree with the body-centred structure of space-group D_{4h}^{17} . To fit the X-ray data there must be forty-four molecules $\text{PbCl}_2 \cdot \text{Cu}(\text{OH})_2$ in the unit cell. The closeness of the a dimensions of boleite and cumengeite allows of the parallel growth of these two minerals. The cubo-octahedral crystals of boleite show only slight optical anomalies, and the so-called "cubic boleite" or pseudo-boleite occurring as simple cubes is distinguished by a higher double refraction in its outer zones. Analysis and the X-ray patterns show that these are really identical, the surface differences being evidently due to an intergrowth with cumengeite.

Boracite.—X-Ray examination of boracite⁵⁵ throws a doubt on the usually accepted formula $\text{Mg}_7\text{Cl}_2\text{B}_{16}\text{O}_{30}$ (of W. Heintz, 1859). The rhombic-dodecahedral crystals are built up of twelve orthorhombic hemimorphic pyramids in such a manner that the twelve (100) faces give the external faces of the composite crystal. The optic axial plane is parallel to the longer diagonal and the polar c -axes are parallel to the shorter diagonal of a dodecahedral face. The positive ends of the polar axes are directed towards alternate pseudo-triad axes, and this gives rise to the well-known pyroelectric properties of the mineral. X-Ray measurements gave for the unit cell dimensions of colourless crystals (d 2.92–2.97) $a = b = 16.97$, $c = 12.00$ Å.; and for greenish crystals (d 2.97–3.10) containing some ferrous iron $a = b = 17.11$, $c = 12.10$ Å. This would give seven (or 7.3) molecules of $\text{Mg}_7\text{Cl}_2\text{B}_{16}\text{O}_{30}$ in the unit base-centred cell, which from considerations of symmetry is improbable. A new analysis leads to a formula $\text{Mg}_{25}\text{Cl}_8\text{B}_{56}\text{O}_{105}$; or more simply $\text{Mg}_6\text{Cl}_2\text{B}_{14}\text{O}_{26}$, eight (7.845) molecules of which can be accommodated in the unit cell. It would be of interest to determine by X-ray

⁵³ B. Gossner, *Amer. Min.*, 1928, **13**, 580; *A.*, 749.

⁵⁴ B. Gossner and M. Arm, *Z. Krist.*, 1929, **72**, 202.

⁵⁵ J. W. Gruner, *Amer. Min.*, 1928, **13**, 481; *Amer. J. Sci.*, 1929, [v], **17**, 453; *A.*, 749.

methods whether the structure is truly cubic at a temperature above 265° .

Domeykite Group.—The several copper arsenide minerals from Michigan have been examined by X-ray methods and by the metallographic method on polished surfaces under the microscope. L. S. Ramsdell⁵⁶ finds that domeykite (Cu_3As) is a definite compound, but it gives a different X-ray pattern from that given by artificial Cu_3As obtained with fused mixtures of copper and arsenic; when heated, however, it changes into a form corresponding with the artificial product. Algodonite (Cu_6As) is also found to be a definite compound, although it cannot be prepared artificially in fusions; when heated, it breaks down into a mixture of Cu_3As and Cu-As solution. Whitneyite (Cu_9As) is a mixture of algodonite and the Cu-As solutions. Arsenic up to 4% can be present in solid solution in copper. F. Machatschki⁵⁷ finds, on the other hand, that both algodonite and whitneyite are mixtures of: (1) a cubic substance which appears to be metallic copper contaminated with arsenic and has a lattice constant $a = 3.647\text{--}3.651 \text{ \AA.}$; and (2) a compound poorer in copper than Cu_6As , possessing the hexagonal type of close-packed structure with lattice constants $a = 2.598\text{--}2.599$, $c = 4.213\text{--}4.215 \text{ \AA.}$

Fahlerz Group.—X-Ray examination of tetrahedrite "from Hungary" by J. Palacios⁵⁸ gave a unit cell of edge $a = 10.39 \text{ \AA.}$ and containing eight molecules Cu_3SbS_3 . W. F. de Jong⁵⁹ obtained for different specimens $a = 10.190\text{--}10.555 \text{ \AA.}$, with eight molecules $\text{Cu}_3\text{SbS}_{3-4}$ in the unit cell. F. Machatschki⁶⁰ also examined material from various localities and found for Cu-Sb fahlerz (tetrahedrite) $a = 10.32 \text{ \AA.}$, which increases to 10.41 when much silver replaces copper, and decreases to 10.19 in tennantite when arsenic takes the place of antimony in the formula $\text{R}^{\text{I}}_3\text{R}^{\text{II}}\text{S}_3$. These authors are all agreed in rejecting the old formula $4\text{Cu}_2\text{S}, \text{Sb}_2\text{S}_3$, but they take no account of the bivalent metals, principally iron and zinc, which are almost invariably present in fahlerz. This mineral shows, in fact, a wide range in chemical composition and in density; but not in a single case were these determined for the materials used for the X-ray analysis. V. V. Nikitin⁶¹ points out a similarity in the atomic structure suggested by Machatschki for fahlerz with those of chalcopyrite and zinc-blende; and he also emphasises the fact that these minerals are often found in parallel growth on crystals of

⁵⁶ *Amer. Min.*, 1929, **14**, 188; *A.*, 1264.

⁵⁷ *Jahrb. Min., Beil.-Bd.*, 1929, [A], **59**, 137.

⁵⁸ *Anal. Fis. Quím.*, 1927, **25**, 248; *A.*, 1927, 1015.

⁵⁹ Proefschrift, Delft, 1928.

⁶⁰ *Norsk Geol. Tidsskr.*, 1928, **10**, 23; *Z. Krist.*, 1928, **68**, 204; *A.*, 1928, 1080.

⁶¹ *Z. Krist.*, 1929, **69**, 482; *A.*, 1263.

fahlerz, due to the similarity, not only of structure, but also of molecular volume. He makes the interesting suggestion that molecules of zinc-blende, chalcopyrite (CuFeS_2), and perhaps metacinnabarite (HgS), may be present in solid solution or even very finely disseminated in the fahlerz substance. This seems to afford a satisfactory explanation of the departure of analyses from the ideal formula Cu_3SbS_3 .

Spinel.—Certain artificial gem spinels differ from ordinary spinel in containing a large excess of alumina over that required by the spinel formula MgAl_2O_4 . These have been studied in detail by F. Rinne⁶² by all the available methods. Each pear-shaped drop is a single crystal and shows rounded faces of the cube, octahedron, and rhombic-dodecahedron, and the silky upper surface shows a minute reticulated crystalline pattern. The axis of the pear, corresponding with the direction of growth under the oxyhydrogen blow-pipe, usually coincides with a cubic axis of the crystal. X-Ray examination by the Laue, rotating-crystal, and powder methods shows no essential difference between these artificial spinels of variable composition and natural spinel; and the powder photographs are the same as those given by $\gamma\text{-Al}_2\text{O}_3$. The following table gives a selection of the determined data:

Composition.	Sp. gr.	n_D .	Edge a of unit cube.
$\text{MgO}, \text{Al}_2\text{O}_3$	3.577	1.7190	8.02 Å.
$\text{MgO}, 1.7\text{Al}_2\text{O}_3$	3.604	1.7239	—
$\text{MgO}, 3.3\text{Al}_2\text{O}_3$	3.620	1.7272	7.96
$\text{MgO}, 4\text{Al}_2\text{O}_3$	3.625	1.7284	7.92
$\text{MgO}, 5\text{Al}_2\text{O}_3$	—	1.7288	7.91

The conclusion reached is that the material consists of a solid solution or mixed crystal of $\gamma\text{-Al}_2\text{O}_3$ in spinel. When spinels that contain an excess of alumina are tempered for some hours at 800° they become cloudy and show a moonstone schiller and asterism, due, as shown under the ultra-microscope, to the separation of minute particles. Tempered for longer periods, the stones become opaque; the Lauegrams then show two series of spots, and thin sections under the microscope show a regular network intergrowth of spinel and corundum. This change is accompanied by an increase in density from 3.62 to 3.81, corresponding with the inversion of $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ (corundum).

Sources of Supply of the Less Common Elements.

Practical uses for more and more elements are gradually becoming known. Detailed accounts of the modes of occurrence and the

⁶² *Jahrb. Min., Beil.-Bd.*, 1928, [A], 58, 43; A., 1928, 730. See also P. F. Kerr, *Amer. Min.*, 1929, 14, 259.

precise localities where the rarer minerals have been found, often by chance, have been recorded in mineralogical literature in a more or less haphazard manner. When any particular element is discovered to have some economic application, there is an immediate call for it, and the mineralogical records, if made available by suitable indexes, should then be of some use. Even for the abundant elements, such as aluminium, a knowledge of the various modes of occurrence and distribution of its several minerals, such as cryolite and bauxite, is of importance.

For the elements already in practical use this aspect of the subject is dealt with in several books on economic geology and ore deposits. A book collecting together the scattered information on the geochemical distribution of the chemical elements has recently been compiled by G. Berg, "*Vorkommen und Geochemie der mineralischen Rohstoffe*" (Leipzig, 1929); and another dealing more with general principles by F. Behrend and G. Berg, "*Chemische Geologie*" (Stuttgart, 1927).

Beryllium.—In view of the possible use of light and strong alloys of aluminium and beryllium in aeronautics, there have been many inquiries for sources of this element. Beryl, the most abundant beryllium mineral (Be about 5%), usually occurs as isolated crystals in certain pegmatite veins, large crystals being occasionally found in the felspar quarries of the south of Norway, and larger crystals weighing one or two tons have been found in New Hampshire. A recent find of large crystals is reported from Namaqualand, South Africa, and a beryl deposit is worked for emeralds of gem quality in the Leydsdorp district, north-eastern Transvaal.⁶³ A new find of massive white beryl, apparently in considerable quantity, is reported in the Masull ravine, near Merano in Trentino.⁶⁴ Other minerals containing a higher percentage of the metal, namely, hambergite (Be 19%), phenakite (16½%), bertrandite (15%), beryllonite (7%), chrysoberyl (7%), and euclase (6%), are of more sparing occurrence; while bromellite, BeO (*Ann. Reports*, 1925, **22**, 277), is known only as a few minute crystals. The old felspar quarry near Písek in Bohemia, which has yielded a variety of beryllium minerals, has recently been reopened.⁶⁵ A list of localities where beryllium minerals have been found is given by M. Hosenfeld.⁶⁶

Bromine.—Carnallite from Solikamsk, govt. Perm, Russia, contains 0.17–0.30% of bromine, apparently present as a double salt

⁶³ J. M. Le Grange, *Trans. Geol. Soc. S. Africa*, 1930, **32** (for 1929).

⁶⁴ E. Dittler, *Tsch. Min. Petr. Mitt.*, 1929, **40**, 188.

⁶⁵ J. V. Želízko, *Věstník Státního Geol. Ústavu Československé Republiky*, 1928, **4**, 23.

⁶⁶ *Wiss. Veröff. Siemens-Konz.*, 1929, **8**, [1], 21; B., 722.

KCl, MgBr₂, 6H₂O. Large amounts appear to be available.⁶⁷ A pamphlet on the production and occurrence of bromine has been issued in the series "The Mineral Industry of the British Empire and Foreign Countries" (Imperial Institute, London, 1928).

Cæsium.—The main source of cæsium, now used in thermionic valves, is the mineral pollucite (Cs₂O 34%). This has been produced in some quantity from the felspar quarries in pegmatite at Andover and other localities in Maine, U.S.A.⁶⁸ In general appearance, pollucite is very similar to quartz, and perhaps it has been overlooked in some other pegmatites. Other cæsium-bearing minerals are cæsium-beryl, rhodizite, and lepidolite; the last, when mined for lithium, may come to be of importance as a source of cæsium. Lepidolite from South-West Africa was found to contain Cs₂O 0.60% with Rb₂O 1.73%.⁶⁹

Germanium.—Many minerals have been examined spectrographically for germanium.⁷⁰ Traces were found in the tin ores cassiterite and stannite, in zinc ores, native copper, and various silicates. Apart from the germanium mineral argyrodite, and germanite, the largest amount (0.1%) was found in enargite from Mexico.

Gallium.—Various minerals have been examined spectrographically for gallium. Lepidolite from California⁷¹ yielded 0.007% of the metal, and a green kaolin⁷² from Japan had contents of the order 0.0004–0.004%.

Hafnium.—A review of the mineralogy of hafnium has been given by O. I. Lee.⁷³ In zirconium minerals the ratio HfO₂:ZrO₂ varies from 0.007 to 0.5 with an average of 0.02.⁷⁴ In zircon, the content of hafnium appears to increase with the radioactivity (due to traces of thorium and uranium), and altered zircons (alvite and crytolite) are richer than unaltered.

Iodine.—In small amounts iodine is of wide distribution (*Ann. Reports*, 1927, 24, 294). It is recorded (I 0.13%) in the saline encrustations of Vesuvius,⁷⁵ in the gases escaping from various

⁶⁷ N. N. Efremov and A. A. Veselovski, *J. Chem. Ind. Moscow*, 1928, 5, 1365; A., 1163.

⁶⁸ E. E. Fairbanks, *Amer. Min.*, 1928, 13, 21.

⁶⁹ J. Jakob, *Schweiz. Min. Petr. Mitt.*, 1927, 7, 139; A., 45.

⁷⁰ J. Papish, F. M. Brewer, and D. A. Holt, *J. Amer. Chem. Soc.*, 1927, 49, 3028; A., 1928, 146; J. Papish, *Econ. Geol.*, 1928, 23, 660; 1929, 24, 470.

⁷¹ J. Papish and D. A. Holt, *J. Physical Chem.*, 1928, 32, 142; A., 1928, 265.

⁷² S. Iimori, *Sci. Papers Inst. Phys. Chem. Res. Tokyo* (Supplement), 1929, 10, No. 8; A., 420.

⁷³ *Chem. Reviews*, 1928, 5, 17.

⁷⁴ G. von Hevesy and K. Würstlin, *Z. physikal. Chem.*, 1928, 139, 605; A., 288.

⁷⁵ L. Coniglio, *Ann. R. Osservatorio Vesuviano*, 1925, [iii], 2, 123.

mineral springs,⁷⁶ and in rock phosphates.⁷⁷ A pamphlet on the production and occurrence of iodine has been issued in the series "The Mineral Industry of the British Empire and Foreign Countries" (Imperial Institute, London, 1928).

Lithium.—Lithium minerals, lepidolite, spodumene, and amblygonite, are found in considerable quantities at several places in the Oiseau River district in Manitoba.⁷⁸

Radium.—A report dealing with the uses of radium, more especially for medical treatment, and with its production and sources of supply has been issued by the Radium Sub-Committee of the Committee of Civil Research (London, 1929). The production from the western American carnotite fell from 35½ g. of radium element in 1921 to 12 g. in 1923 and has now ceased. The present restricted supply is obtained from the richer uranium ore associated with copper ores in Katanga, Belgian Congo. A recent discovery of pitchblende in the Gordonia district of Cape Province as isolated crystals (uraninite) in pegmatite is less promising than would be a lode deposit with large mammillated masses of pitchblende. The copper belt now being explored in Northern Rhodesia is perhaps a likely place for future developments. All igneous rocks contain minute amounts of radium; for example, C. S. Piggot⁷⁹ finds in granites from the eastern United States from 0.378 to 4.826×10^{-12} g. of radium per gram of rock.

Rubidium.—A method for the extraction of rubidium salts from carnallite has been given by G. Jander and H. Faber.⁸⁰ J. Jakob⁶⁹ records the presence of Rb_2O 1.73% in lepidolite from South-West Africa, and 1.16% has been found in lepidolite from Japan.⁸¹

Ruthenium.—This is present as a minor constituent of pink kaolin from Tanokami, Japan, the colour of which is supposed to be due to the presence of rhodium and ruthenium.⁸²

Selenium.—The use of photo-sensitive cells for television and the transmission of pictures is calling for an increased supply of this element. A new occurrence of selenium minerals has been found in the Roter Bär mine at Andreasberg in the Harz Mountains,

⁷⁶ T. von Fellenberg, *Biochem. Z.*, 1928, **193**, 384; *A.*, 1928, 611.

⁷⁷ E. Wilke-Dörfurt, J. Beck, and G. Plepp, *Z. anorg. Chem.*, 1928, **172**, 344; *A.*, 1928, 864.

⁷⁸ J. S. De Lury, *Industrial Development Board of Manitoba, Winnipeg*, 1927.

⁷⁹ *Amer. J. Sci.*, 1929, [5], **17**, 13; *A.*, 1936.

⁸⁰ *Z. anorg. Chem.*, 1929, **127**, 321.

⁸¹ S. Iimori and J. Yoshimura, *Bull. Chem. Soc. Japan*, 1926, **1**, 237; *A.*, 1927, 129.

⁸² *Idem, ibid.*, 1929, **4**, 1; *A.*, 420.

analyses of the picked ore showing Se 24—27%.⁸³ The selenium ores from the earlier known occurrences in the Harz Mountains⁸⁴ have been studied by the metallographic method in polished sections under the microscope.⁸⁵ A new selenium mineral has been detected, and named klockmannite (CuSe),⁸⁶ in intimate association with the umangite (Cu_3Se_2) of the Sierra de Umango in Argentina, Lehrbach in the Harz Mountains, and at Skrikerum in Sweden. Selenium in a form soluble in water, perhaps as selenious acid or as an alkali selenite, has been found in saline encrustations (Se 1.25% with Te 0.04%) in the crater of Vesuvius.⁸⁷

New Minerals.

An eleventh dictionary list of new mineral names for the period 1926—1928 gives 190 names, several of which are merely synonyms or of little value.⁸⁸ Some rare minerals of the platinum group, of which a preliminary mention was made in the last report (1927, 24, 311) have now been more fully described. Potarite, PdHg , discovered by the late Sir John Harrison, crystallises as octahedra in the cubic system.⁸⁹ Palladium antimonide, Pd_3Sb , from the Transvaal platinum fields has been named stibiopalladinite.⁹⁰ Another new platinum mineral from the same district is listed below under the name cooperite. Several new crystallised iron sulphates are described from a mine in Arizona, where a body of pyritic ore had been burning underground for some years; they were probably formed when the mine was flooded with water in the attempts to extinguish the fire.⁹¹

Bismutotantalite,⁹² tantalate (and niobate) of bismuth, $\text{Bi}_2\text{O}_3 \cdot (\text{Ta}, \text{Nb})_2\text{O}_5$, as large orthorhombic crystals in a pegmatite vein on Gamba Hill, Uganda. Analyses show Bi_2O_3 about 50%.

⁸³ H. Rose, *Fortschr. Min. Krist. Petr.*, 1927, 12, 72; W. Geilmann and H. Rose, *Jahrb. Min., Beil.-Bd.*, 1928, [A], 57, 785.

⁸⁴ Selenium was extracted on a moderately large scale from these ores at Tilkerode in the eastern Harz a hundred years ago, and the product appears to have been marketed in the form of small medallions showing in relief a bust of Berzelius. Examples of these are preserved in the apartments of the Chemical Society and in the Mineral Department of the British Museum (L. J. Spencer, *Min. Mag.*, 1928, 21, 404).

⁸⁵ G. Frebold, *Centr. Min.*, [A], 1927, 16, 196.

⁸⁶ P. Ramdohr, *Centr. Min.*, [A], 1928, 225; *A.*, 289.

⁸⁷ F. Zambonini and L. Coniglio, *Ann. R. Osservatorio Vesuviano*, 1925, [iii], 2, 3.

⁸⁸ L. J. Spencer, *Min. Mag.*, 1928, 21, 556.

⁸⁹ *Idem*, *ibid.*, p. 397; *A.*, 1928, 612.

⁹⁰ P. A. Wagner, "The Platinum Deposits and Mines of South Africa," Edinburgh and London, 1929, p. 12; H. Schneiderhöhn, *Centr. Min.*, [A], 1929, 193.

⁹¹ C. Lausen, *Amer. Min.*, 1928, 13, 203.

⁹² E. J. Wayland and L. J. Spencer, *Min. Mag.*, 1929, 22, 185.

Ta_2O_5 31—41%, Nb_2O_5 14—6%, and the mineral is analogous to stibiotantalite ($\text{Sb}_2\text{Ta}_2\text{O}_8$). If the formula is written as $(\text{BiO})_2\text{Ta}_2\text{O}_6$ and the axial ratios are readjusted, the mineral shows a close relation to tantalite ($\text{Fe}_2\text{Ta}_2\text{O}_6$). The black crystals are in part altered to a pinkish-yellow hydrated material which seems to consist of a mixture of two minerals.

Cooperite,^{90, 93} sulpharsenide of platinum, $\text{Pt}(\text{As,S})_2$, as minute steel-grey fragments and rectangular rods found in the concentrates from the platiniferous norites and dunites of the Bushveld, Transvaal. Examined by reflected polarised light, it is seen to be anisotropic and probably orthorhombic. It presumably belongs to the marcasite group and is dimorphous with sperrylite (PtAs_2). Like sperrylite, it is attacked neither by aqua regia nor by nascent chlorine (when the mineral is treated with solid potassium chlorate and hydrochloric acid). After ignition the material yields to aqua regia.

Gudmundite,⁹⁴ sulphantimonide of iron, FeSbS , as small silver-white to steel-grey crystals embedded in calcite. The orthorhombic crystals are isomorphous with mispickel (FeAsS), and the two minerals, very similar in appearance, are associated together in the lead and zinc ore at Gudmundstrop, near Sala, Sweden.

Hydrothorite,⁹⁵ hydrous thorium silicate, $\text{ThSiO}_4 \cdot 4\text{H}_2\text{O}$, occurring, together with thorogummite and pilbarite, as an alteration product of mackintoshite in a pegmatite vein at Wodgina, Western Australia. It is pale pink or cream-coloured, earthy, and very friable, and is optically isotropic.

Larnite,⁹⁶ calcium orthosilicate, occurring as a constituent of a metamorphic rock at the contact of chalk and dolerite near Larne in County Antrim. The finely granular rock shows an unusual assemblage of minerals, including spurrite ($2\text{Ca}_2\text{SiO}_4 \cdot \text{CaCO}_3$), larnite (Ca_2SiO_4), merwinite ($3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$), gehlenite, spinel, and calcite. Larnite is monoclinic with optical characters agreeing with those of the artificial $\alpha\text{-Ca}_2\text{SiO}_4$. When the larnite rock is heated to dull redness and allowed to cool, it falls to powder, due to the inversion to $\gamma\text{-Ca}_2\text{SiO}_4$.

Larsenite and *Calcium-larsenite*.⁹⁷ These two minerals occur in veinlets in the massive zinc ore at Franklin Furnace, New Jersey. Larsenite is an orthosilicate of lead and zinc, PbZnSiO_4 , and forms

⁹³ R. A. Cooper, *J. Chem. Met. Min. Soc. S. Africa*, 1928, **28**, 281; *A.*, 1928, 1111.

⁹⁴ K. Johansson, *Z. Krist.*, 1928, **68**, 87; *A.*, 788.

⁹⁵ E. S. Simpson, *J. Roy. Soc. W. Australia*, 1928, **13** (for 1927), 37.

⁹⁶ C. E. Tilley, *Min. Mag.*, 1929, **22**, 77; *A.*, 787.

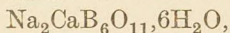
⁹⁷ C. Palache, L. H. Bauer, and H. Berman, *Amer. Min.*, 1928, **13**, 142, 334; *A.*, 787.

colourless orthorhombic prisms isomorphous with olivine. In calcium-larsenite about half of the lead is replaced by calcium, the formula being $(\text{Pb,Ca})\text{ZnSiO}_4$. This massive white mineral is remarkable in showing a brilliant lemon-yellow fluorescence when exposed to ultra-violet rays. It is intimately associated with willemite, hardystonite, and clinohedrite, and in the mass these minerals are scarcely distinguishable, but in the ultra-violet rays they show fluorescent glows respectively brilliant green, violet, and orange-red.⁹⁸ This property enabled pure material to be selected for analysis. Larsenite displays a pale violet fluorescence.

Mitscherlichite,⁹⁹ hydrous double chloride of potassium and copper, $\text{K}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$, as minute greenish-blue crystals on the surface of a saline stalactite from the floor of the crater of Vesuvius. The crystals are tetragonal like those of the artificial salt prepared by E. Mitscherlich in 1840.

Nahcolite,¹ sodium hydrogen carbonate, not previously definitely recognised as a mineral, is so named from the formula NaHCO_3 , to distinguish it from the other sodium carbonate minerals. It occurs as a constituent of a white crystalline saline encrustation found in 1888 on the walls of a Roman conduit at the Baths of Nero, which was exposed during the construction of the railway line from Baia to Naples. When the conduit was opened the contained atmosphere was highly charged with carbon dioxide. Analysis of the material shows varying amounts of sodium carbonate and sulphate with 7.48–8.45% of H_2O , and they are interpreted as mixtures of thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), nahcolite (NaHCO_3), and thenardite (Na_2SO_4), each of which was also determined by its optical characters.

Probertite,² hydrous borate of sodium and calcium,



as rosettes of glassy columnar monoclinic crystals embedded in kernite and secondary borax in the Kramer district, Kern Co., California. Probertite (also known as kramerite) and kernite (or rasorite) are the primary minerals in a lode-like deposit formed by hot springs in Miocene beds. Secondary minerals derived from them are borax and ulexite.

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⁹⁸ C. Palache, *Amer. Min.*, 1928, 13, 330; L. J. Spencer, *ibid.*, 1929, 14, 33.

⁹⁹ F. Zambonini and G. Carobbi, *Ann. R. Osservatorio Vesuviano*, 1925, [iii], 2, 7.

¹ F. A. Bannister, *Min. Mag.*, 1929, 22, 53; *A.*, 535.

² A. S. Eakle, *Amer. Min.*, 1929, 14, 427.

